156 Topics in Current Chemistry

Photoinduced Electron Transfer I

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With 40 Figures and 12 Tables

Springer-Verlag Berlin Heidelberg NewYork
London Paris Tokyo Hong Kong

This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

As a rule, contributions are specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers are accepted for "Topics in Current Chemistry" in English.

ISBN 3-540-52379-0 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-52379-0 Springer-Verlag New York Berlin Heidelberg

Printed in GDR

Bookbinding: Lüderitz & Bauer, Berlin
2151/3020-543210 – Printed on acid-freepaper

Guest Editor

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Preface to Volume I

When planning this series, which is composed of about twenty single contributions, the guest editor was not aware of the problems that would arise while fitting them together in the desired order, always trying to minimize time between submission and printing. Therefore I am grateful to the authors who allowed me to combine their contributions which are mainly devoted to "Photoinduced Electron Transfer (PET) In Organic Chemistry".

After a historical introduction of PET and its fundamentals, in the first two chapters, the following contributions cover some elementary reactions, i.e. bond cleavage, as well as oxygenations and PET of charged species. The last two chapters turn to applications which are currently being extensively studied in research as well as in the chemical industry. Photoimaging technologies are discussed in the final contribution and may be taken as an example for photochemical methods which are essential in industrial applications.

I hope that these articles show the high potential of PET and that the reader will find stimulation for his own work. Possibly, as a consequence, interest in the following volumes will be aroused.

Münster, December 1989 Jochen Mattay

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Preface to Series on Photoinduced Electron Transfer

The transfer of an electron from a donor molecule to an acceptor molecule belongs to the most fundamental processes in artificial and natural systems, although, at the primary stage, bonds are neither broken nor formed. However, electron transfer determines the chemical fate of the molecular entities to a great extent. Nature has made use of this principle from the early beginnings of life by converting light energy to chemical energy via charge separation. In recent years, man has learnt, e.g. from X-ray analyses performed by Huber, Michel and Deisenhofer, how elaborately the molecular entities are constructed within the supermolecular framework of proteins. The light energy is transferred along cascades of donor and acceptor substrates in order to prevent back electron transfer as an energy wasting step and chemical changes are thus induced in the desired manner.

Today we are still far from a complete understanding of light-driven electron transfer processes in natural systems. It is not without reason that the Pimental Report emphasizes the necessity of future efforts in this field, since to understand and "to replicate photosynthesis in the laboratory would clearly be a major triumph with dramatic implications". Despite the fact that we are at the very beginning of knowledge about these fundamental natural processes, we have made much progress in understanding electron transfer reactions in "simple" molecular systems. For example, most recently, a unified view of organic and inorganic reaction mechanisms has been discussed by Kochi. In this context, photochemistry plays a crucial role not only for the reasons mentioned above, but also as a tool to achieve electron transfer reactions. The literature contains a host of examples, inorganic as well as organic, homogeneous as well as heterogeneous. Not surprisingly, most of them have been published within the last decade, although early examples have been known since the beginning of photochemistry (cf. Roth's article). A reason is certainly the rapid development of analytical methods, which makes possible the study of chemical processes at very short time ranges. Eberson in his monograph, printed by this publishing company two years ago, nicely pointed out that "electron transfer theories come in cycles". Though electron transfer has been known to inorganic chemists for a relatively long time, organic chemists have still to make up for missing concepts (cf. Eberson).

A major challenge for research in the future, the "control of chemical reactions" as stated by the Pimentel Report, can be approached by various methods; light-driven processes are among the most important ones. Without interaction of the diverse scientific disciplines, recent progress in photochemistry, as well as future developments would scarcely be possible. This is particularly true for the study of electron transfer processes. In this context lies a challenge for science and economy and the special fascination of this topic – at least for the guest editor.

The scope of photochemistry and the knowledge about the fundamentals of photoinduced electron transfer reactions have tremendously broadened over the last decade, as have their applications. Therefore I deeply appreciate that the Springer-Verlag has shown interest in this important development and is introducing a series of volumes on new trends in this field. It is clear that not all aspects of this rapidly developing topic can be exhaustively compiled. I have therefore tried to select some papers which representatively reflect the current state of research. Several important contributions might be considered missing by those readers who are currently involved in this field, however, these scientists are referred to other monographs and periodical review series which have been published recently. These volumes are meant to give an impression of this newly discovered reaction type, its potential and on the other hand to complement other series.

The guest editor deeply appreciates that well known experts have decided to contribute to this series. Their effort was substantial and I am thankful to all of them. Finally, I wish to express may appreciation to Dr. Stumpe and his coworkers at the Springer-Verlag for helping me with all the problems which arose during the process of bringing the manuscript together.

Münster, December 1989 Jochen Mattay

A Brief History of Photoinduced Electron Transfer and Related Reactions

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Photoinitiated electron transfer reactions are among the earliest photochemical reactions documented in the chemical literature and (ground state) electron donor-acceptor interactions have been known for over one hundred years. Some aspects of plant photosynthesis were already known to Priestly in the eighteenth century. The photooxidation of oxalic acid by metal ions in aqueous solution was discovered by Seekamp (U^{VI}) in 1805 and by Döbereiner (Fe^{III}) in 1830. The electron donor-acceptor interactions between aromatic hydrocarbons and picric acid were noticed by Fritzsche in the 1850s; the quinhydrones are even older,

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having been described by both Wöhler (1800–1882) and Laurent (1807–1853). One-electron reductions (e.g. of benzil by potassium) were carried out by Laurent in 1835, a one-electron oxidation (of chrysene by sulfuric acid) by Liebermann in 1871. The development of photoinitiated electron transfer from the observation of a few isolated and poorly understood examples to its current status as a highly sophisticated, interdisciplinary branch of science is delineated.

1 Introduction

Photo-induced electron transfer reactions occupy a central position in the chemistry of life. The photoreactions of the living plant have produced the oxygen in the Earth's atmosphere, provide nourishment for higher forms of life, and have laid the foundation for seemingly inexhaustible energy resources. Yet, the relatively complex nature of these processes did not reveal itself readily to humankind: as recently as two hundred years ago, essentially no photoreactions were known and photosynthesis in the living plant remained a mystery. Even the great A. L. Lavoisier (1743–1794), to whom we owe so many insights into the nature of chemistry, veiled his understanding of light and of the chemical reactions caused by it in philosophical eloquence: "By means of light, the benevolence of the Deity has filled the earth with organization, sensation, and intelligence. The fable of Prometheus might perhaps be considered as giving a hint of this philosophical truth even to the ancients [1]."

In this article, we discuss several early examples of photoinitiated electron transfer reactions. We also follow the development of alternative methods to achieve one-electron oxidation and reduction. This general reaction type, of which the photo-induced reaction is a special case, pervades organic, bio-, and inorganic chemistry.

2 Priestley and Photochemistry in the Eighteenth Century

Lavoisier's English contemporary Joseph Priestley (1733–1804; Fig. 1) was the first to encounter simple light-induced conversions, including the production of "dephlogisticated air" by green plants. In the course of his experiments on "different kinds of air" he used a twelve inch lens to focus sunlight on a variety of samples in a closed vessel (Fig. 2). For example, he exposed partially filled vials containing "spirit of nitre" (nitric acid) to sunlight and observed that the liquid assumed a reddish color [2]. In follow-up experiments he established that the reddish product (nitrogen dioxide) was formed in the vapor phase and then dissolved in the liquid. "Being now satisfied that it was the action of light upon the vapour of spirit of nitre that gave it color, I amused myself with throwing a strong light, by means of a lens, into the upper part of a phial, the lower part of which contained spirit of nitre [2]." Although this reaction formally amounts to a *reduction*, it is best understood as a light induced bond homolysis.

$$\mathrm{HO{-}NO_2} \xrightarrow{h\nu} \mathrm{HO^{\cdot}} + {}^{\cdot}\mathrm{NO_2}\,.$$

Another experiment involved conversion of mercury to a red solid with an increase in weight and a diminution of the gas volume [3]. This pioneering

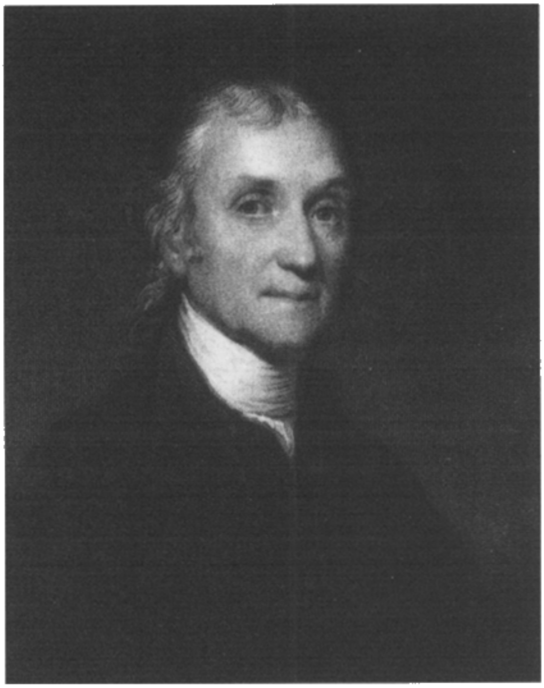

Fig. 1. Joseph Priestley (1733–1804), engraving by W. Hall – "From a picture by Gilbert Stewart" Printed by C. Knight, London

experiment was described and interpreted correctly by Lavoisier as a combination of mercury with oxygen, i.e. as an *oxidation* [3]. In view of the known gas phase photochemistry of mercury one might consider this conversion a photoreaction. However, the experimental evidence indicates that this solid-to-solid conversion is a thermal reaction; the focussed sunbeam only serves as a heat source, as was the custom from as early as 1599 [4].

Perhaps the most important photoreaction observed and studied by Priestley was the photosynthesis of the green plant [5, 6]. In his own words, he "fully

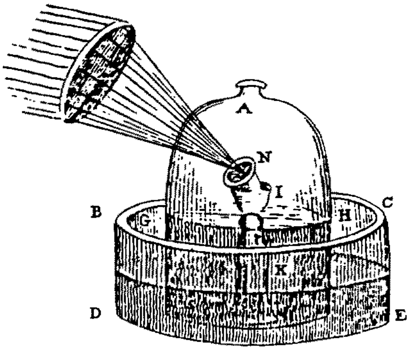

Fig. 2. Apparatus for carrying out calcinations, credited to Priestley [3]. The metal is contained "in a porcelain cup N, placed upon the stand IK, under a jar A, in the basin BCDE, full of water: the water is made to rise up to GH by sucking out the air with a syphon, and the focus of a burning glass is made to fall upon the metal

ascertained the influence of light in the production of *dephlogisticated air* (oxygen) in water by means of a *green substance*". He first believed that the gas evolution was due to a light-induced reaction of water [5]. However, in later experiments he noticed the presence of green matter, and a colleague identified tiny plants under a microscope [6].

After learning of Priestley's early experiments, Jan Ingenhousz, a Dutch physician who practiced in England and Austria, carried out experiments of his own. He determined that the action of light on plants "improves" air and that Priestley's "green matter" must be a plant [7]. Nicholas Theodore de Saussure (1767–1845) advanced the problem in 1804, when he grew plants in enclosed spaces that allowed him to monitor changes in the gas content quantitatively. He demonstrated that the influence of light causes plants to consume water and carbon dioxide and to generate oxygen [8]. Thus, the macroscopic changes accompanying photosynthesis had been established early in the nineteenth century. However, despite the best efforts of leading scientists such as Liebig [9], Baeyer [10], or Willstätter [11], more detailed insights, specifically the crucial role of electron transfer, were not achieved until well into the twentieth century.

To appreciate this time-lag, it is useful to recall that the electron was not recognized as an elementary particle until the twentieth century. Electron beams had been known as *cathode rays* since 1876, but their *corpuscular* nature was recognized only in 1897 [12]. The term *electron* was introduced in 1891 to designate the fundamental unit of electricity, namely the electric charge of a hydrogen ion [13]. Only later was it applied to Thompson's *corpuscules*, and it achieved general acceptance with Millikan's quite accurate determination of the electronic charge by the oil drop method [14, 15].

3 Photoinduced Electron Transfer in the Nineteenth Century

The photosynthetic reaction center is a highly complex array of functional moieties designed and arranged by nature in a superstructure that optimizes the overall efficiency of charge separation. In contrast, the reaction partners in most other electron transfer reactions are chosen by investigators who either emulate nature or pursue the photoreactions of molecules or systems conceived and synthesized by man.

Early in the nineteenth century, Seekamp reported the interesting observation that certain organic substances are decomposed in the presence of uranium salts under the influence of light [16]. This reaction also attracted attention [17] because it was one of the first, which was recognized as temperature independent, an important finding for recognizing the nature of photoreactions. Although different mechanisms can be envisioned, electron transfer is a major reaction path, resulting in oxidation of the organic substrate and reduction of the uranium ion. For example, Fay investigated the photoreaction of uranyl compounds in the presence of oxalic and other organic acids. He identified formic acid in addition to CO_2

[18]. The reaction of uranyl oxalate has been applied for actinometric determinations [19, 20].

Another electron transfer experiment in a system designed by man was carried out by J. W. Döbereiner in 1831. Döbereiner prepared an aqueous solution containing oxalic acid and iron(III) oxide and exposed it to sunlight in a small glass bulb. He observed evolution of tiny gas bubbles and precipitation of a solid, and was able to identify the gas as CO_2 and the precipitation as a basic iron(II) oxide, known as Humboldtite [21]. Döbereiner found similar reactions for the salts of Pt, Ag, Ir, and ruled out the correponding dark reactions by careful control experiments.

$$Fe^{+++} + (CO_2^-)_2 \xrightarrow{h\nu} Fe^{++} + CO_2^- + CO_2 .$$

The reader may have recognized Döbereiner's system as the basis of ferrioxalate actinometry [22, 23]. Indeed, this system was utilized throughout the nineteenth century in numerous efforts to determine the energy of solar radiation [24–32], giving rise on more than one occasion to disagreements and arguments about its merits and its most appropriate application.

Despite its "popularity" in the nineteenth century, Döbereiner's prototype electron transfer reaction remained an isolated incident. To the best of this reviewer's knowledge, no other light-induced electron transfer reactions were uncovered until after the turn of the century. The principal photoreactions observed in the second half of the nineteenth century were dimerizations and isomerizations; only a few abstraction reactions had come to light [33]. On the other hand, several one-electron redox reactions suitable for the generation of radical ions were discovered and some knowledge about molecular complexes was accumulated. Knowledge about radical ions would prove crucial for the ultimate understanding of electron transfer processes, as it allowed the recognition of the primary intermediates generated in these reactions.

4 Chemical Redox Reactions in the Nineteenth Century

Laurent was the first to react a carbonyl compound, benzil, with an alkali metal. These attempts were more eventful than successful: instead of the first radical anion he observed spontaneous ignition [34]. Some fifty years later, Beckmann and Paul were more successful, when they reacted aromatic ketones (benzophenone) and diketones (benzil) with sodium [35]. They noted the sensitivity of the solutions and of the colored solid products to air and moisture and worked in a hydrogen atmosphere. Although they demonstrated admirable laboratory skills, (cf. Fig. 3), they did not understand the nature of the colored intermediates.

The structure of this species was recognized twenty years later by Schlenk and co-workers [36, 37], who suggested that the intensely colored and highly air sensitive products constitute a new class of trivalent-carbon compounds [36]. Schlenk

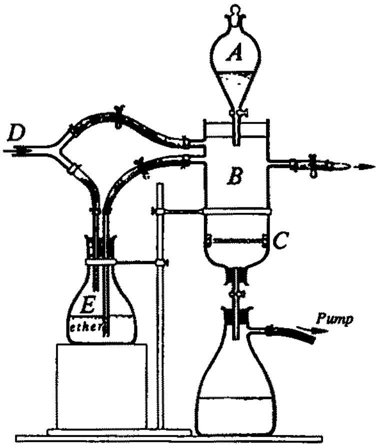

Fig. 3. Apparatus for the reaction of alkali metals with carbonyl compounds and for the separation of the solid adducts (adapted from Beckmann and Paul [31]). A, separatory funnel in which the reaction is carried out; B, cylinder with inert atmosphere; C, perforated porcellain disc with filter paper, held in place by cork rings; D, entry of inert gas (H_2 or CO_2) from Kipp apparatus; E, wash ether reservoir

proposed the term "metal ketyls" to represent the composition and (by the suffix "yl") the "radical nature" of these substances. Later, conductivity [38] and magnetic susceptibility measurements [39, 40] as well as electron spin resonance since the 1950s revealed complex equilibria between radical anions, dissociated ("free") or paired with alkali ions, and (dimeric) pinacolate ions.

A radical anion of an aromatic hydrocarbon was implicated as early as 1866, when Berthelot obtained a black dipotassium salt from naphthalene and potassium [41]. This reaction must have proceeded via the naphthalene radical anion as a more or less fleeting intermediate. Again, Schlenk and co-workers captured the essence of such an intermediate. In the case of anthracene they noticed the existence of two different species, a purple dianion and a blue transient species with a banded spectrum [42]. They identified this intermediate as a "monosodium addition product which contains trivalent carbon". Further details were revealed only with the advent of electron paramagnetic resonance spectroscopy.

The nineteenth century also produced reagents for the one-electron oxidation of suitable substrates. For example, sulfuric acid was employed for many years as an "analytical reagent" because of some color reactions. Thus, Laurent treated "benzimid", $C^{28}H^{10}O^{2}+HAz$, a residue from the *oil of bitter almonds* (benzaldehyde) and observed an indigo blue solution [34]. On the other hand, the blue solution observed by Liebermann upon treatment of chrysene with sulfuric acid can be attributed to the chrysene radical cation [43].

In the twentieth century, Kehrmann applied this reagent for the one- and two-electron oxidation of phenothiazine and characterized "semiquinoid" and "holoquinoid" species by UV/VIS spectroscopy (Fig. 4) [44, 45]. In the 1950s colored solutions of aromatic hydrocarbons (perylene, anthracene, etc.) in sulfuric acid were found to be paramagnetic [46] and, shortly thereafter, their radical cations were postulated based on optical [47] and ESR spectroscopic data [48]. The detailed reaction mechanisms of these oxidations are still in question; molecular oxygen may well be a necessary ingredient.

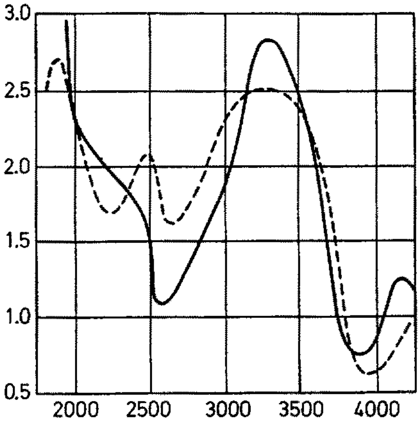

Fig. 4. Optical spectra of "holoquinoid" (———) and "meriquinoid" (– – –) *N*-methyl-phenazonium ions in ethanol [adapted from Hantzsch A (1916) Ber. Dtsch. Chem. Ges. 49: 511]

The halogens were also used as oxidizing reagents; bromine in particular has proved quite useful. It was employed in 1879 on di- and tetramethyl-*p*-phenylenediamine, [49–51] and Wieland used it to generate numerous aminium salts derived from triarylamines and tetraarylhydrazines [52, 53].

5 Electron Donor Acceptor Complexes

The history of organic radical ions is intertwined with the history of "quinhydrones", molecular aggregates between substrates that are readily oxidized and compounds that are readily reduced. In the absence of modern analytical methods, particularly magnetic resonance techniques, it was often difficult to ascertain whether one was dealing with a homogeneous radical ion salt, such as Wurster's Blue, or with a quinhydrone, such as the prototypical complex formed between benzoquinone and benzohydroquinone. Indeed, in several cases radical ions were mistaken for molecular complexes [54, 55]. Furthermore, there are instances where a "free" radical ion and a molecular complex have a similar appearance, at least subjectively, so that it is not clear which of the two species was observed originally.

We illustrate the sometimes conflicting results with several experiments involving the diketone benzil, originally prepared by Liebig and Wöhler. Since neither the quadrivalence of carbon nor its proper atomic weight had been established, the compound was described as the "radical" benzoyl with a composition of $C^{28}H^{10}O^{2}$. Laurent treated the new compound with potassium tartrate and observed a "rose colored solution" [34]. It is plausible that this reaction leads to the semidione in analogy to the formation of semiquinones under similar conditions.

On the other hand, Scholl showed in 1899 that the color reaction requires the presence of traces of benzoin [56], an impurity which Laurent might have overlooked. Accordingly, the colored species might be a "quinhydrone" and it was identified as such by Weissberger et al. [57]. To complicate matters further, Klinger reported another type of molecular complex resulting from the light-induced partial reduction of benzil in wet ether [58, 59]. He identified a colorless solid with the composition

$$2\,C_{14}H_{10}O_4+C_{14}H_{12}O_4\,.$$

Clearly, the available evidence neither rules out nor establishes unambiguously any of the proposed structures.

Among the early donor-acceptor complexes the quinhydrones deserve a special place, because they may well be the first such complexes and because their *composition* was the subject of a controversy more than one hundred years ago [60–64]. Once the composition was clarified, the debate could center on the *structural* details. Willstätter's assignment of two fully equivalent components [65] is incompatible with the finding that neither D nor ^{14}C was exchanged between the components [66–67]. On the other hand, mere hydrogen bonding [68], cannot explain the deep color. The best representation of these structures involves both hydrogen bonding and charge transfer (EDA resonance) [69].

Carl Julius Fritzsche (1808–1871) deserves credit for pioneering work on donor-acceptor complexes. During his thirty five year tenure at the Academy in Petersburg (1834–1869), he carried out detailed investigations of the components of coal tar. In the course of these experiments, as early as 1857, he observed and characterized 1:1 molecular complexes of picric acid with benzene, naphthalene, and anthracene [70, 71]. Remarkably, Fritzsche already understood these aromatics as a series of homologs:

$$C_4H_4 + C_8H_2\,, \qquad C_4H_4 + 2\,C_8H_2\,, \quad \text{and} \quad C_4H_4 + 3\,C_8H_2;$$

once again, the discrepancy with today's formulation is due to an incorrect atomic weight for carbon.

Fritzsche also used charge transfer complexes with picric acid to characterize the photodimer of anthracene [72] and he also observed colored complexes between aromatic hydrocarbons and anthraquinones and nitroanthraquinones. He had obtained these substances, without recognizing their nature, in an attempt to nitrate anthracene. Ten years after Fritzsche's publications, Berthelot carried out detailed investigations on numerous picrates of aromatic hydrocarbons and delineated applications of these complexes for the identification and separation of aromatic hydrocarbons [73, 74].

Charge transfer complexes received much attention in the early decades of the twentieth century [75] and again in the 1950s and 1960s [76]. They would prove to be of particular importance because the excitation of charge transfer absorptions allows the unambiguous generation of "intimate" radical ion pairs.

Excited state complexes are relevant in connection with photo-induced electron transfer, since their formation frequently competes with or precedes electron transfer. The simplest examples, excited state dimers (*excimers*), were discussed by Kautsky as early as 1939 [77]. The first organic excimer, the dimer of pyrene, was identified by its characteristic, red-shifted, structureless emission spectrum by

Förster and Kasper in 1954 [78]. However, it should be noted that an inorganic excimer, the He dimer, anteceded the organic one by almost 25 years [79].

Nine years later, Leonhardt and Weller detected an excimer type emission in solutions containing perylene and dimethylaniline [80]. This first *heteroexcimer* has become the prototype of an ever expanding area of research. Perhaps the impact of these observations are best illustrated by the monograph dealing with the new phenomenom published only 12 years after the first report [81]. The significance of this research for the proper understanding of photo-induced electron transfer is born out by the first positive identification of a radical anion resulting from the irradiation of a donor-acceptor system in polar solvents (vide infra) [82].

6 Photoionization

An important method for the generation of radical ions relies on the effects of high energy radiation, including γ- or X irradiation and electron beams, upon glassy matrices. This method utilizes the fact that high-energy photons cause ejection of highly energetic electrons from appropriate target (matrix) materials. The high-energy electrons, in turn, excite and ionize molecules present in the same system. The earliest experiments of this type were carried out by Goldstein with cathode rays [83–86]. Originally, he observed persistent colorations (*Nachfarben*) upon irradiation of inorganic materials, such as alkali halides. Later on, he observed similar effects when he subjected organic salts, including tetramethyl and tetraethyl ammonium chloride, to the same treatment [86]. Similarly, Wieland exposed crystalline tetraarylhydrazines to electron bombardment at liquid air temperatures [87]. The resulting strong colorations persisted for minutes and were attributed plausibly to free diarylaminyl radicals.

Thirty years later, these experiments were continued by G. N. Lewis with Lipkin [88] and Bigeleisen, [89] who found that optical irradiation with a mercury arc lamp resulted in three different types of photoreactions: generation of two neutral radicals (termed *photo-dissociation*); generation of a positive and a negative ion, (*photo-ionization*); and ejection of an electron (*photo-oxidation*). The spectrum of the solvent-trapped electron resulting from the photo-ejection process was first observed by Linschitz [90].

The application of radiolysis as a method to generate organic radical ions from matrix isolated materials was pioneered by Hamill [91–93]. Although the chemical effects of ionizing radiation are highly complex, this method has been applied successfully for many radical anions as well as cations. The nature of the resulting species is determined by the matrix and the choice of substrate. A variety of halogen-containing matrix materials is available, among them tetrachloromethane, the chlorobutanes, and several freon mixtures. Electron ejection from these materials results in highly unstable radical cations which, in turn, oxidize appropriate solute molecules at concentrations as low as 1 in 10^3, regenerating the matrix material. Optical spectroscopy and electron spin resonance spectroscopy are the techniques employed most frequently to characterize the transient reaction products.

7 Photoinduced Electron Transfer in the Twentieth Century

We suggest that the foundations of photo-induced electron transfer as a viable field of scientific investigation were not laid by a single investigator or by any one school. Rather, the 1920s and 1930s brought a gradual awakening to the idea of electron transfer, originating from rather diverse fields of study and featuring many individual contributions. We refer to several pioneering studies, dealing with: potential mechanisms of fluorescence quenching; photosensitization; the inhibition of light and dark reactions [94, 95] including those proceeding by chain mechanisms [96]; and the mechanism of plant photosynthesis. As early as 1923, Weigert had postulated that the primary photochemical process in photosynthesis is an electron transfer reaction (from chlorophyll to oxygen) [97]. Later, Rabinowitch and Weiss studied in vivo photo-reactions of ethyl chlorophyllide and found that the green pigment was reversibly oxidized in light, while ferric chloride was reduced [98].

Baur discussed the process of fluorescence quenching as a "molecular electrolysis" and noted that "all desensitizers, inhibitors, and fluorescence quenchers are substances with well defined redox potentials [99–101]". Weiss contributed several studies [102–105] in which he clearly recognized electron transfer as an important step in deactivating an excited state: "Fluorescence quenching in solution can be considered as a simple electron transfer process [102]." Interestingly, he already used a *donor-acceptor* designation [104] albeit in a manner different from today's familiar usage. In his formulation, the term *donor* designated the photo-excited molecule creating a positive charge in the quencher (*acceptor*).

$$D^* + \mathrm{Acc} = D^- + \mathrm{Acc}^+ .$$

In 1945, Rabinowitch described the energetics of electron transfer reactions qualitatively as follows: "An electronically excited molecule has an increased tendency to give away an electron, as well as a capacity for acquiring an electron to replace the one which was removed from its normal level [106]". The quantitative formulation of this conclusion is known today as the Rehm-Weller equation [107]. Ultimately, the involvement of electron transfer processes in fluorescence quenching was confirmed experimentally by the observation of the previously characterized absorption spectrum of perylene anion following the quenching of perylene fluorescence by *N,N*-disubstituted anilines [78] although the corresponding anilinium radical cations remained undetected.

The current detailed understanding of photo-induced electron transfer processes has been advanced dramatically by the development of modern spectroscopic methods. For example, the application of time-resolved optical spectroscopy has developed from modest beginnings (flash-phyotolysis with millisecond resolution) [108, 109] to the current state of the art, where laser spectroscopy with nanosecond resolution [110–113] must be considered routine, and where picosecond [114–116] or even femtosecond resolution [117] is no longer uncommon. Other spectroscopic techniques that have been applied to the study of electron transfer processes include time-resolved Raman spectroscopy [118], (time resolved) electron spin

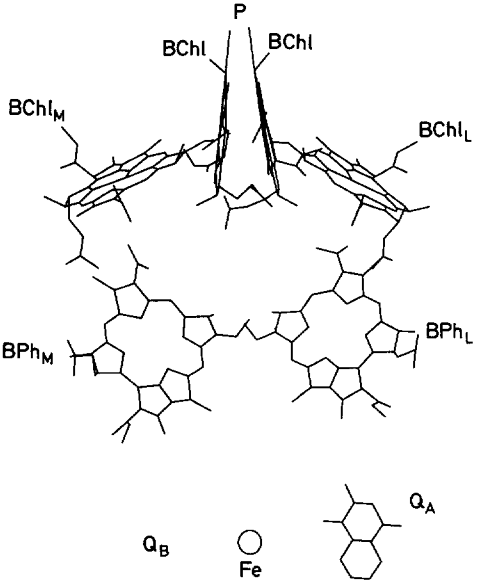

Fig. 5. Arrangement of the essential components of *Rhodopseudomonas viridis* reaction center determined by X-ray crystallography [131], reproduced from Wasielewski MR, Tiede DM (1986) FEBS Lett. 204: 368

resonance spectroscopy (TR-ESR) [119], and steady-state [120, 121] and time resolved [122] chemically induced dynamic nuclear polarization (CIDNP). These methods have provided a wealth of information about the rates of primary processes and the identity of primary reaction intermediates. Concurrently, a keen interest has developed in the manifold chemical reactions initiated by electron transfer processes [123–125] and in the various structure types of the intermediates [126].

The current understanding of plant and bacteriophotosynthesis has been advanced dramatically by several developments. Among these are the isolation of photosynthetic reaction centers, for example, of the purple bacterium *Rhodobacter sphaeroides* [127], the magnetic characterization of "special" pairs [128–130] and, ultimately, the detailed X-ray crystallographic delineation of the complete reaction center of *Rhodopseudomonas viridis* (Fig. 5) [131]. The reaction transforming light energy into chemical potential occurs in a pigment-protein complex ("reaction center") via a series of rapid electron transfer steps. Within one nanosecond, it produces a charge-separated state comprising an oxidized electron donor and a reduced electron acceptor. These accomplishments have expanded our understanding of the photosynthetic process to a sophisticated, remarkably detailed level.

8 Free Energy Relationship and Electron Transfer Theory

In the view of many, the theoretical contributions of Marcus have earned a special place in the electron transfer field [132, 133]. Over three decades ago, Marcus formulated the rate of an electron transfer reaction as a function of two parameters: a) its driving force, i.e. the free energy, ΔG^0, of the reaction, and b) a "solvent reorganization energy", λ_s, required to accommodate the changing charge distribution.

$$k_{ET} = A' \exp - [(\Delta G^0 + \lambda_s)^2 (4\lambda_s k_B T)^{-1}] .$$

The most striking result emerging from this work was the prediction that electron transfer rates increase with increasing driving force to a maximum, at $\lambda_s = \Delta G^0$, but then unexpectedly (and perhaps counterintuitively) decrease upon further increases in driving force. The essential predictions of this theory were reproduced by numerous theoretical approaches descending from the original idea of Marcus [134]. It took almost thirty years before this prediction was finally confirmed by experiment.

For the purpose of this discussion, electron transfer reactions are conveniently divided into three categories: 1) charge separation, the generation of radical ion pairs from a photoexcited molecules and a suitable ground state molecule of complementary nature; 2) charge recombination, the reverse process regenerating two neutral ground state molecules; and 3) (charge-neutral) electron exchange between a charged and a neutral moiety. Only the charge separation reaction meets the strict definition of the title. However, in view of the overall importance of all three reaction types and because of unifying features we will touch on all of them.

The energy dependence of *charge separation* is most readily scrutinized and it was investigated first in considerable detail. Rehm and Weller studied rate constants of fluorescence quenching for a series of more than 60 organic donor-acceptor pairs and found a maximum rate of electron transfer, essentially diffusion limited, without any indication for an "inverted" region (Fig. 6) [136]. These results were at variance with the existing theories, but they could be rationalized on the basis

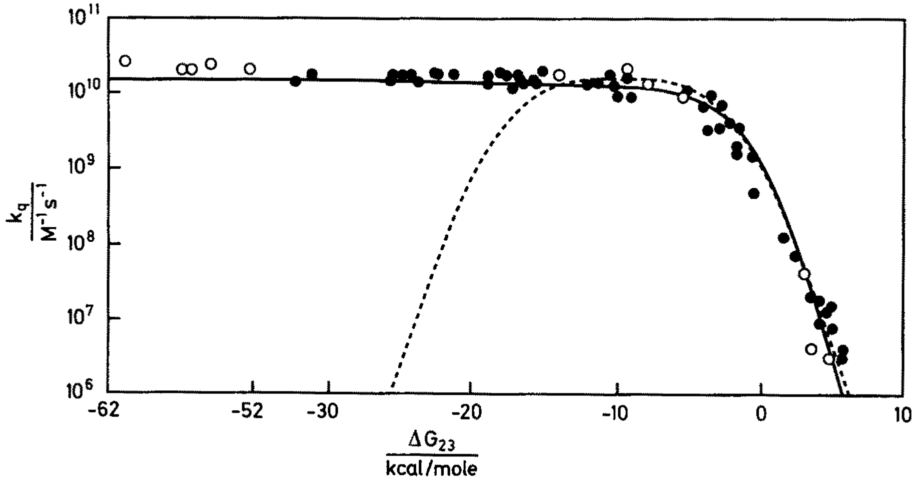

Fig. 6. Fluorescence quenching rate constants as a function of the free enthalpy, ΔG^0, for the electron transfer process from a donor to an excited acceptor (●) or from an excited acceptor to a donor (○) [136]

of an ad-hoc theory [136]. Similar results were observed in a plethora of additional systems, including organometallic systems. All attempts to verify the predicted "inverted" free energy dependence of electron transfer rates met with failure [134, 137].

The first indication for any reduction of the electron transfer rate with increasing driving force was observed by Miller and coworkers [135]. Recognizing problems that might affect electron transfer rates in fluid solution, particularly diffusion limited rates and complex formation, they studied the (charge neutral) electron transfer from radiolytically generated radical anions to aromatic hydrocarbons in frozen solutions. These reactions covered free energy changes ranging from $-\Delta G^0 = 0.01$ to 2.75 eV, and the rates of electron transfer were found to decrease at high exothermicities [135].

The analysis of the above data is based on a random distance distribution between donor and acceptor, an assumption, that cannot be confirmed (or even probed) readily. Accordingly, these experiments were extended to intramolecular electron transfer in a series of molecules of the general type A-Sp-B, in which two potential acceptors are linked by the rigid 5α-androstan skeleton. The electron transfer rates observed for the radiolytically generated monoanions of these systems showed a striking deviation from the classical Brønsted relationship (Fig. 7) [138, 139]. They unambiguously confirm predictions of the electron transfer theories [134] descending from the original idea of Marcus.

The Marcus "inverted" region for *charge recombination* was first reported by Wasielewski [140] and elaborated elegantly by Gould, Farid, and coworkers [141]. These studies include an elegant elucidation of the differences between "solvent

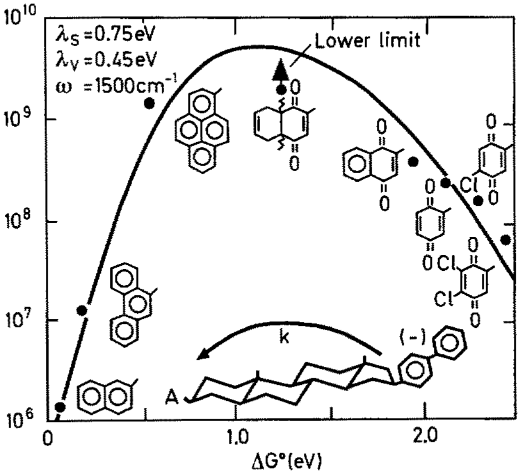

Fig. 7. Intramolecular rate constants as a function of free energy change in 2-methyloxacyclopentane solution at 296 K. The electron transfer occurs from biphenyl anions to the eight different acceptor moieties (shown adjacent to the data points), in eight bifunctional molecules of the general structure shown in the center. Reprinted with permission from J. Am. Chem. Soc. 106: 3047. Copyright (1984) American Chemical Society.

penetrated" and "contact" radical ion pairs [142]. Most recently, a *charge separation* reaction was also found to exhibit the full range of behavior predicted by Marcus' theory [143].

Photolysis of substituted naphthylmethyl phenylacetates, of the general structure $X-Np-CH_2-O-(C=O)-CH_2-Ph$, yields products resulting from both ionic and radical intermediates. The products can be analyzed by a complex reaction scheme, including a sequence of steps initiated by bond homolysis, generating radical pairs, $X-Np-CH_2^{\cdot}\ {}^{\cdot}O-(C=O)-CH_2Ph$, and followed by electron transfer, generating ion pairs, $X-Np-CH_2^{+}\ {}^{-}O-(C=O)-CH_2Ph$. Based on a numerical analysis of the isolated product yields, the rates of the competing reactions can be assigned. Appropriate substitution of the naphthyl moiety affects the oxidation potential of the naphthylmethyl radical, causing characteristic changes in product yields and, accordingly, in electron transfer rates. The calculated rates fall between $10^{8.8}$ (4-CN−Np) and $10^{10.8}$ (4-Me−Np) and decrease toward higher driving forces [143].

Although they cannot be considered primary photo-reactions, we mention briefly the special category of electron return (charge annihilation) reactions which give rise to molecular triplet states. As early as 1961, Leonhardt and Weller observed the triplet-triplet absorption of perylene following flashlamp excitation in the presence of *N*,*N*-diethylaniline [82]. The "simultaneous" observation of the perylene anion (vide supra) suggested recombination of triplet radical ion pairs. A decade later, Ottolenghi and coworkers carried out similar experiments with improved time resolution (15 nsec laser excitation) and observed "prompt" triplet formation upon excitation of anthracene or pyrene in the presence of *N*,*N*-diethylaniline. Since the rapid formation of the triplet seemed to preclude a recombination mechanism, the authors postulated intersystem crossing in exciplexes [144, 145].

A possible mechanism for the intersystem crossing of ion pairs on the required (nanosecond) time scale was first suggested by G. N. Taylor. He studied the quenching of aromatic hydrocarbon excited singlet states by the isomeric 1,2-dicyanoethylenes and observed characteristic nuclear spin polarization (CIDNP) effects for the quencher and its geometric isomer [146]. Taylor recognized that the rearranged product was generated from the dicyanoethylene triplet state and concluded that this state was populated by charge annihilation of triplet ion pairs. Hyperfine induced singlet-triplet mixing, the key process underlying the induction of CIDNP effects, can cause intersystem crossing on a time scale of 1−10 nanoseconds.

The involvement of hyperfine induced singlet-triplet mixing was confirmed for the reaction of pyrene with 3,5-dimethoxy-*N*,*N*-dimethylaniline by analyzing the magnetic field dependence of the optically detected triplet yield [148]. At a field of 500 Gauss, the yield of fast triplets was reduced to about 80% of its value at the Earth's magnetic field (0.5 G, "zero field"). The application of CIDNP spectroscopy has brought to light information about a variety of triplet states, which are populated by charge annihilation of triplet radical pairs [149]. These systems have in common that the triplet state can decay either to the starting material or to a geometrical or valence isomer. This feature ensures an efficient spin sorting process and allows a well resolved observation of the polarization patterns.

9 Perspective

The field of light-induced electron transfer remains in a state of rapid development in many of the areas on which this brief history has touched and in others that could not be included here. Exciting progress is being made in the delineation of the *first picosecond* of photosynthesis, in further characterizing photosynthetic reaction centers, in the area of artificial models. The dependence of intramolecular electron transfer upon distance, solvent, orientation is being delineated. Many of these developments are detailed in the following chapters.

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Fundamental Concepts of Photoinduced Electron Transfer

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Table of Contents

Photoinduced electron transfer (PET) is a term reserved to describe the transfer of an electron between photoexcited and ground-state molecules. The energetics and dynamics of PET are shown to depend on the structure of the reactants, the distance separating the reactants,

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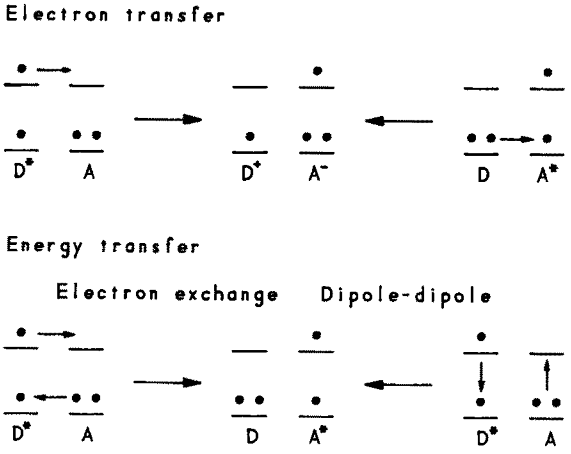
the nature and polarity of the medium, and Coulombic effects. The dynamic interplay of these parameters gives rise to a variety of intermediates, including short-lived Franck-Condon intermediates, exciplexes, contact ion pairs, solvent-separated radical ions, and free ions. An understanding of the spin dynamics of PET can be helpful in sorting out various charge intermediates. The rate of PET is explored on the basis of the classical Marcus-Hush theory and nonclassical, quantum mechanical theories. Special attention is given to the role of electronic and nuclear barriers. A discussion of various procedures used to maximize the efficiency of ion-pair formation is presented, with attention to recent examples.

1 The Scope of Photoelectron Transfer

One of the remarkable achievements of photochemistry has been the recognition that certain molecules on photoexcitation become powerful electron donors or acceptors. This phenomenon known as photoinduced electron transfer (PET) has attracted the interest of chemists from many fields. In organic chemistry, for example, interest in PET has uncovered novel pathways for the synthesis of organic molecules [1, 2]. Inorganic chemists have applied PET to development of solar energy storage and conversion systems, utilizing transition metal complexes [3]. Molecular biologists are investigating photosynthesis and electron-transport in biological systems on the basis of simple models of PET [4]. There have also been interesting proposals to design "molecular computing devices" using the concept of PET [5].

The seminal work of Marcus and Hush has had a significant impact on the development of PET. Pioneering efforts by Sutin, Hopfield, Jortner, and others established the connection between thermal electron transfer and photoelectron transfer [6]. This work set the stage for a notable series of experiments where laser flash spectroscopy [7], chemically induced nuclear polarization [8], resonance Raman spectroscopy [9], time-resolved microwave conductivity [10], and time-resolved photoacoustic calorimetry [11], to site only a few examples, have been successfully employed to chart the dynamics of PET in homogeneous solution, the solid-state, and organized assemblies.

In PET, an electron migrates between a photoexcited and ground-state species. According to this concept, PET can be classified as a quenching pathway. In fact, like quenching by energy transfer, PET may involve a dynamic interaction between a photoexcited state and neighboring ground-state species:



Scheme 1

D and A are the conventional designations of a donor and acceptor. In electron transfer, the excited state, identified by the star, can be an electron donor or acceptor; in energy transfer, the excited state is exclusively an energy donor. Energy transfer can operate by a dipole-dipole (Coulombic) mechanism involving the mutual interaction of electrons. Since mutual contact between the reactants is not required, the dipole-dipole mechanism can be operative over large distances, sometimes greater than 50 Å. Energy transfer by electron exchange, however, requires a closer approach of the reactants to allow for the mutual exchange of electrons. In this respect, energy transfer by electron exchange is similar to electron transfer. On the other hand, efficient energy transfer requires that the excited-state energy of D exceeds that of A. In electron transfer, the energetics are dictated by the redox potentials of D and A, as well as the energy of the excited state.

There are other characteristics which distinguish electron from energy transfer, but this comparison will not be the subject of this paper. Instead, the objective in this article will be to introduce the reader to the fundamentals of PET. The overall pathway in PET can be summarized as shown in Scheme 2:

$$D^m + A^n \xrightarrow{h\nu} D^{m*} + A^n \rightarrow D^{m+1} + A^{n-1} \leftarrow D^m + A^{n*} \xleftarrow{h\nu} D^m + A^n\,. \tag{2}$$

The reactants may be neutral (m, n = 0) or charged species (m, n $\neq$ 0). For simplicity, we have temporarily overlooked many details of PET in Scheme 2. For example, decay pathways and chemical transformations have not been shown.

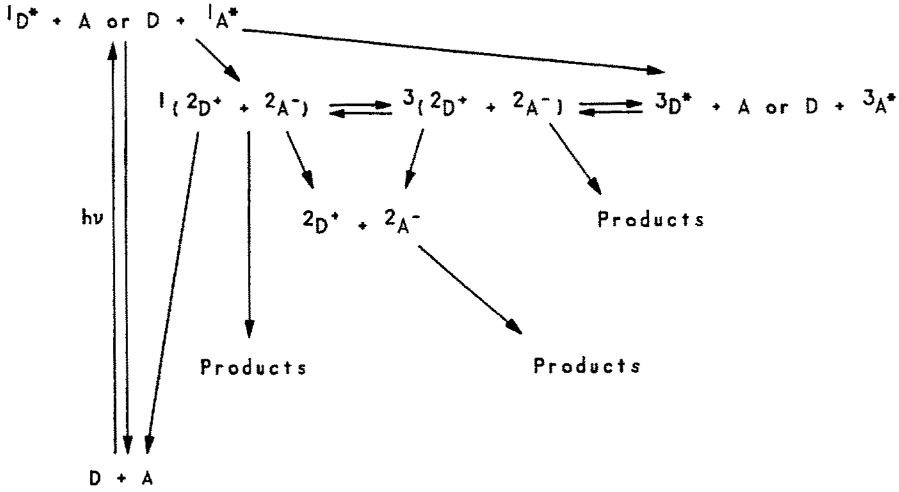


Fig. 1. An archetypal representation of the major pathways in PET. In PET, the quenching of neutral singlet or triplet excited states leads to singlet and triplet ion pairs, respectively. These ionic spin states may interconvert, dissociate in solution to free and solvated ion radicals, or undergo chemical transformations. Free energy increases upward on the vertical axis

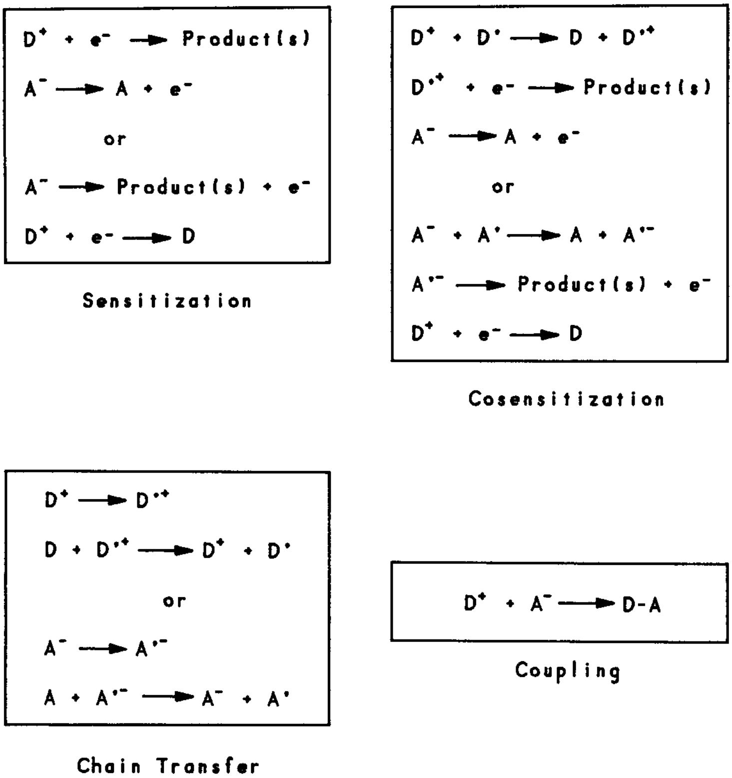
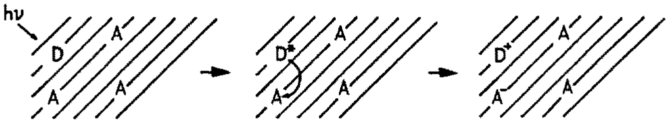


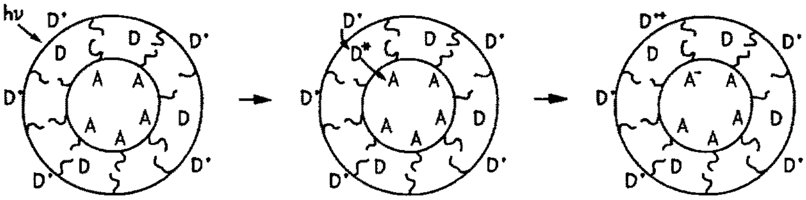
Fig. 2. PET can generate reactive ion radicals. The pathways shown in this diagram are typical examples. In photosensitization, the excited state (the sensitizer) is eventually recovered for another reaction. Coupling reactions usually take place between ions in close proximity

Nor have we specified electronic spin, and we have not yet indicated that the donor and acceptor may be linked together within the same molecular structure. These features of PET will be covered in this paper.

The scope of PET encompasses a diverse range of reactions in homogeneous and heterogeneous environments. Figure 1 depicts the pathways of PET in solution involving neutral singlet and triplet donor excited states. For illustrative purposes, we assume that the excited molecule is an electron donor, a practice to be followed in this article. These pathways proceed "downhill" on an energy scale. Electron transfer leads to singlet or triplet ion pairs, which subsequently undergo electron transfer to ground-state reactants (electron return), recombination to triplet states of either reactant, or ion dissociation. Ion pairs may also undergo a series of reactions where the excited state is eventually recovered, free to participate in further reactions [1, 2, 12]. These reactions belong to the group of photochemical reactions known as *photosensitizations by electron transfer*. There are also



PET in the Solid State



PET in an Organized Assembly

Fig. 3. PET takes place in a variety of environments. An electron may tunnel between reactants randomly dispersed in solid materials or in frozen media. In organized assemblies, the donor and acceptor molecules can be arranged in the medium in a variety of ways, depending on the molecular structures and charges of the reactants as well as the molecular structure of the environment. The representation shown in this figure is only suggestive of the many possible arrangements

cosensitizations involving two sensitizers, coupling reactions, and chain transfers [1, 2, 13]. Figure 2 classifies photoelectron transfers according to these pathways.

PET may take place between donor and acceptor molecules located in heterogeneous or solid environments (Fig. 3), or linked together by a flexible chain or rigid spacer group (Fig. 4). Appropriate examples of these systems and their theoretical and practical ramifications will be presented in this paper.

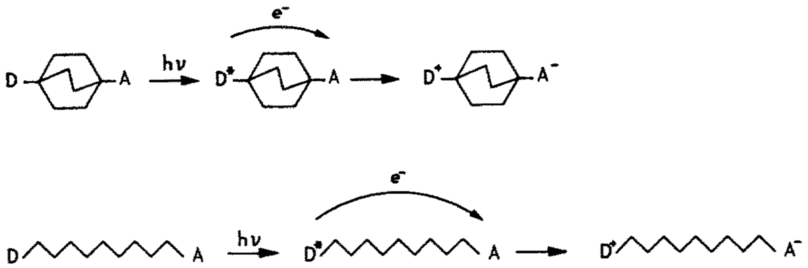


Fig. 4. Schematic showing intramolecular PET. The donor and acceptor may be held together on the same rigid molecule, or they may be linked to a flexible chain. The dynamics of intramolecular PET are strongly influenced by the nature of the linking spacer molecule

2 Ion Pairs and Exciplexes

2.1 Energetics

The property describing the binding force of an electron to a nucleus is the *ionization potential, IP*, which is the energy required to remove an electron from an atom or molecule in the gas phase. The *electron affinity*, EA, is the energy released when an electron combines with an atom or molecule. On the basis of these definitions, electron transfer is feasible when the electron affinity exceeds the ionization potential:

$$\Delta E = IP - EA \tag{3}$$

where ΔE is the change in energy accompanying the electron transfer. In Eq. (3), the parameters can be expressed in electron volts, eV, where one eV is the energy gained by an electron as it accelerates through a potential field of one volt.

When a molecule absorbs a photon, its ionization potential may decrease and its electron affinity may increase. Thus,

$$IP^* = IP - E_{00} \tag{4}$$

and

$$EA^* = EA + E_{00} \tag{5}$$

where E_{00} is the zero-zero electronic energy of an excited-state. For the case where the excited state is an electron donor:

$$\Delta E = IP^* - EA = IP - EA - E_{00} . \tag{6}$$

Similarly, when the excited state accepts an electron, we obtain

$$\Delta E = IP - EA^* = IP - EA - E_{00} . \tag{7}$$

The magnitudes of IP and EA are dictated by the ordering of the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals (Koopman's theorem, Fig. 5). On this basis, electrons in low-energy orbitals, e.g. those residing in σ-bonds, are not as easily abstracted as electrons in non-bonding *n*-orbitals or those occupying higher energy orbitals. Similarly, positive "holes" in low-energy orbitals accept electrons more readily than vacant higher energy orbitals.

Equations (6) and (7) are intended only to test the feasibility of PET for a given pair of donor and acceptor molecules in the gas phase. Because these equations do not account for electrostatic effects or solvation energies due to ion pairing, they cannot be applied with much confidence to PET in solution or solid environments where significant solvation and Coulombic interactions may take

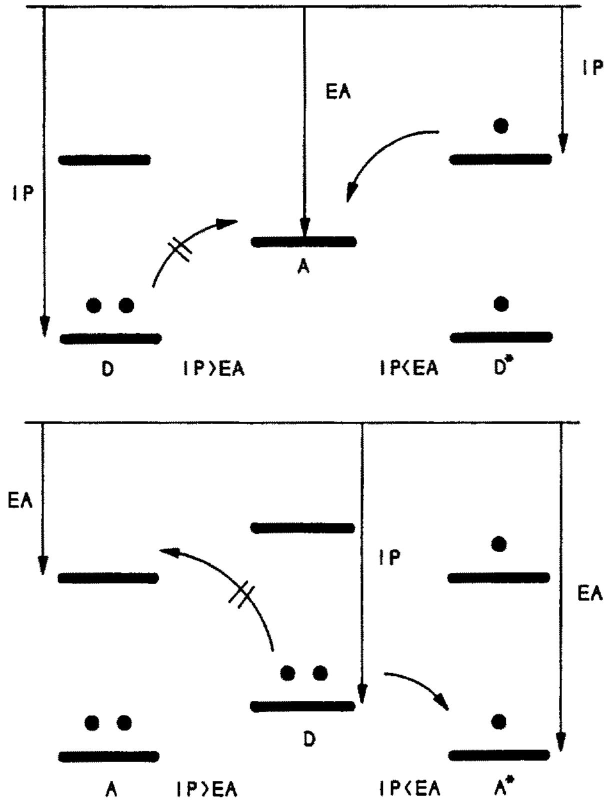


Fig. 5. The feasibility of PET is dictated by the relative energies of donor and acceptor electrons. In this simplified orbital picture, the electrons occupying orbitals can move to other orbitals depending on their ionization potentials (IP) and electron affinities (EA). IP and EA are related to orbital energies by Koopman's theorem

place. To derive more precise thermodynamic expressions, we need to consider the molecular structures of the reactants, their charges, their mobilities, the distances separating the reactants, and the polar nature of the environment. These effects are discussed in the next section.

2.2 Solution Dynamics

We consider the general case where 1. the excited-state species is an electron donor; 2. the reaction takes place in solution; and 3. the reactants are free to diffuse to encounter distances.

In photoelectron transfer, the interaction between an excited- and ground-state molecule creates a series of short-lived ion-pair intermediates, each possessing a unique geometry and electronic distribution. The excitation energy is rapidly dissipated throughout the reactant and solvent molecules as each ion-pair intermediate is successively transformed into another intermediate of lower energy.

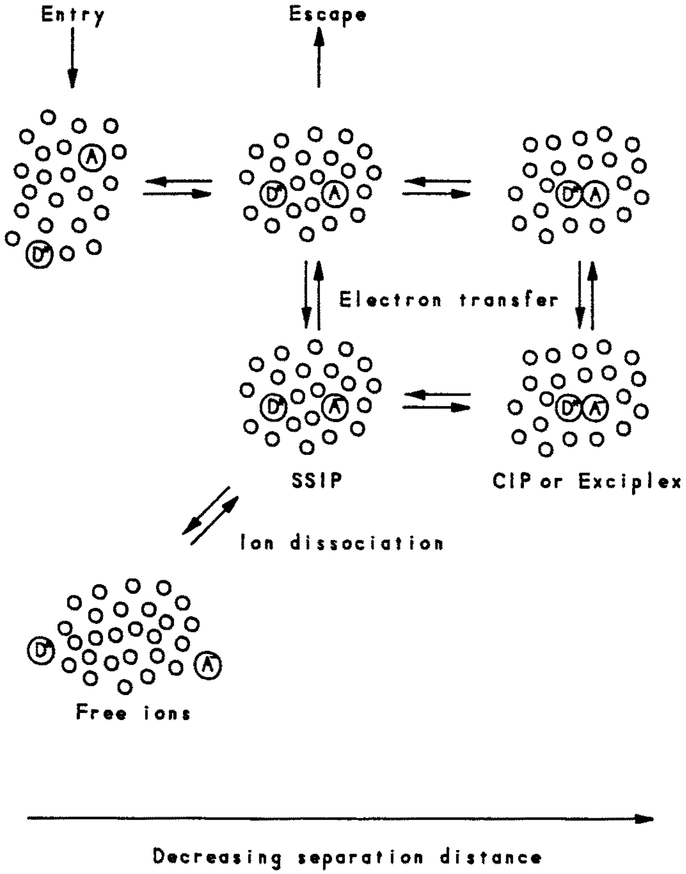


Fig. 6. A diagram showing the dynamic interconversion of solvent-separated ion pairs (SSIP, exciplexes, contact ion pairs (CIP), and free ions in solution. Electron transfer takes place within a cage of solvent molecules to generate a SSIP or more intimate charge-transfer complex, the latter being an exciplex or CIP. The nature of the charge-transfer intermediate generated may depend on the distance separating the reactants. The distance depends on the molecular structures of the reactants, i.e., their sizes, shapes, and steric features. Free ions are produced by ion dissociation from the solvent cage

Electrostatic and solvation effects may stabilize each ion-pair intermediate depending on its structure, the separation distance, and the polarity of the medium. Thus, in solution, the nature of the pathway leading to ionic intermediates is dictated to a large extent by the polarity of the solvent as well as the shape of the excited- and ground-state reactants. Spherical reactants may diffuse into a solvent cage and remain for a short time within an encounter distance (Fig. 6). The separation distance within the cage depends in a complex fashion on the shapes and sizes of the molecules. Typically, for spherical reactants, the center-to-center distance, d_{cc}, may range between ~6.5 and ~7.5 Å. Planar molecules and oblate spheroidal or ellipsoidal molecules can probably approach to closer distances depending on the dimensions of their subaxes.

If several solvent molecules are positioned between the reactants, electron transfer may lead to a high-energy, short-lived Franck-Condon state. Nuclear relaxation of the vibrational modes and solvent modes rapidly produces a relaxed pair of geminate ions, which we describe as a *solvent-separated ion pair (SSIP)*, to highlight the close association that the ion pair shares with the surrounding solvent molecules. In the solvent-separated ion pair, the partners of an ion pair may be separated by one or two solvent molecules (Fig. 6). The driving force of electron transfer leading to a solvent-separated pair is given by Eq. (8) [14]:

$$\Delta G_{SSIP} = IP - EA - \Delta G^* + \Delta G_{sol} + w_P - w_R \tag{8}$$

where

$$\Delta G_{sol} = \Delta G(D^{m+1}) + \Delta G(A^{n-1}) = -\frac{e^2}{2}\left(\frac{1}{r_D} + \frac{1}{r_A}\right)\left(1 - \frac{1}{\varepsilon_s}\right) \tag{9}$$

and w is a "work" term for electrostatic interactions in the reactant (R) and product (P) states, i.e.,

$$w = \frac{z_D z_A e^2}{d_{cc}\varepsilon_s}. \tag{10}$$

The expression given in Eq. (10) for the work assumes that $\mu = 0$, where μ is the ionic strength of the medium. ΔG^* is the free-energy of the equilibrated excited-state ($\Delta G^* \sim \Delta E_{00}$), r_D and r_A are the molecular radii of the donor and acceptor molecules, ε_s is the static dielectric constant or permittivity of the solvent, and z is the charge on each ion. ε_s is related to the response of the permanent dipoles of the surrounding solvent molecules to an external electrical field. Equation (9), the Born equation, measures the difference in solvation energy between radical ions in vacuo and solution.

The IP and the oxidation potential, $E^0(D^+/D)$, of the donor are linearly related:

$$IP = E^0(D^+/D) - \Delta G(D^+) + \text{constant}. \tag{11}$$

Similarly, there is a linear relationship between EA and the reduction potential, $E^0(A/A^-)$, of the acceptor:

$$EA = E^0(A/A^-) + \Delta G(A^-) + \text{constant}. \tag{12}$$

Combining Eqs. (8), (9), (10), (11), and (12) leads to the Rehm-Weller equation [15]:

$$\Delta G_{el} \sim \Delta G_{SSIP} = E^0(D^+/D) - E^0(A/A^-) - \Delta G^* + w_P - w_R. \tag{13}$$

By expressing IP and EA as redox potentials, we have now included terms for the energy of solvation of each solvent-separated ion. Equation (13) is intended to classify PET on the basis of energetics, and consequently can be useful in

Table 1. Calculated free energies of excited-state electron transfers[a]

Donor	Acceptor	ΔG^*	$E^0(D^+/D)$	$E^0(A/A^-)$	ΔG_{el}
norbornadiene	$^3[CA]^*$	2.7	1.54	0.02	−1.24
indene	$^1[CN]^*$	3.88	1.52	−1.98	−0.44
indene	$^3[CN]^*$	3.45	1.52	−1.98	−0.01
$[Ru(bpy)_3^{2+}]^*$	MV^{2+}	2.12	1.29	−0.45	−0.44
$Ru(bpy)_3^{2+}$	$[Cr(bpy)_3^{3+}]^*$	1.71	1.29	−0.26	−0.16
$[Rh_2(dicp)_4^{2+}]^*$	MV^{2+}	1.69	0.89	−0.45	−0.41
TMB	$[Rh_2(dicp)_4^{2+}]^*$	1.69	0.32	−1.4	0.09

[a] Data based on tables in Ref. [2] and references therein; values in eV obtained in acetonitrile, H_2O, or other polar solvents; redox potentials are reported *vs.* standard calomel electrode; calculation of ΔG_{el} performed with Eq. (13). Abbreviations: CA = chloranil; CN = 1-cyanonaphthalene; bpy = 2,2′-bipyridine, MV^{2+} = methylviologen; dicp = 1,3-diisocyanopropane; and TMB = *N,N,N′,N′*-tetramethylbenzidine

distinguishing between electron transfer and other pathways such as quenching by energy transfer (in energy transfer, the electronic energy of the energy donor should exceed the energy of the energy acceptor). Photoinduced electron transfers can be classified as endergonic ($\Delta G_{el} > 0$) or exergonic ($\Delta G_{el} < 0$). Table 1 lists representative redox potentials and free energies for a selected group of reactants in polar solvents on the basis of Eq. (13). These values are intended to demonstrate the wide range of free energies in PET.

It should be noted that the Coulombic term in Eq. (13) is valid only to the extent that the ions are treated as point charges, i.e., $d_{cc} > r_D + r_A$. For PET between neutral reactants, Eq. (13) implies that in nonpolar solvents, electrostatic effects are more important, resulting in greater Coulombic stabilization of the product ions. Polar solvent molecules, however, can reduce Coulombic attraction by "shielding" the electrostatic attraction which exists between the positive and negative ions. Thus, in acetonitrile, a polar solvent with $\varepsilon_s = 37$, the Coulombic term is ~0.03 eV for $d_{cc} \sim 7$ Å, in contrast to a value of ~0.3 eV in a nonpolar solvent where $\varepsilon_s = 4$. These values suggest that ion dissociation into free and solvated radicals is more favorable in polar solvents where the energy barrier for ion separation is not as high as in nonpolar solvents where the ions are held more tightly together.

In a recent article, Suppan has suggested that for neutral reactants a more realistic model of PET may embody an actual collision of the reactants to give a *contact ion pair (CIP)* [16]. Once electron transfer has occurred, the positive and negative ions are rapidly brought together by favorable Coulombic forces. Suppan proposes that $w_P = -e^2/4d$ be used in Eq. (13) for highly polar media ($w_R = 0$ for neutral reactants). Then Coulombic stabilization is more pronounced in polar solvents. For example, with Suppan's Coulombic term, ΔG_{el} is calculated to be −1.69 eV for the electron transfer between triplet chloranil and nonbornadiene (Table 1).

In the conventional view of PET, reactants are visualized as forming collision complexes within the solvent cage prior to electron transfer. The nature of the ionic products is dictated by the structure of the reactants and the polarity of the solvent medium. For example, the encounters between some transition metal complexes can be treated as collisions between two spheres, leading to CIP's. Examples may also include planar molecules, such as aromatic and porphyrin systems, which may generate intimate *charge-transfer complexes* designated as *exciplexes*. Some planar molecules may be capable of approaching to collision distances with interplanar distances of ~3 to 4 Å. There may be strong orbital interactions between these planar reactants, favoring the formation of exciplexes with large binding energies.

By charge-transfer, we mean that an electron is partially shared by both ions. Charge-transfer has a different meaning than electron transfer, in the sense that "electron transfer" usually implies a "complete" transfer of an electron. Operationally, the charge-transfer complex is a distinct and short-lived intermediate. If the charge-transfer complex displays light emission, it is called an exciplex. The center-to-center distance between the two partners within an exciplex is usually approximated as the sum of their molecular radii, i.e., $d_{cc} \sim r_D + r_A$. The same holds true for CIP's. Because of their charge-transfer character, many exciplexes (and CIP's) are predicted to have high dipole moments.

The wavefunction of an exciplex can be written as

$$\Psi_{EX} = c_1\psi(D^*A) + c_2\psi(DA^*) + c_3\psi(D^+A^-) \tag{14}$$

where the coefficients c_1, c_2, and c_3, describe the relative contributions of each wavefunction to the total character of the exciplex. If energy transfer is not important, i.e., $E_{00}(D) < E_{00}(A)$, and the exciplex forms via the transfer of charge, then $\Psi_{EX} \sim c_1\psi(D^*A) + c_3\psi(D^+A^-)$. Such an exciplex can display emission, the yield and lifetime of which are strongly dependent on the polarity of the solvent. The wavefunction for a highly polar, nonemitting exciplex is $\Psi_{EX} \sim c_3\psi(D^+A^-)$. This exciplex has strong CIP character and possesses a large dipole moment. In fact, it is not uncommon for photochemists to designate a nonemitting exciplex as a CIP.

The formation of a CIP or an exciplex may begin with a collision between the donor and acceptor resulting in a vibrationally excited ion-pair intermediate. Eventually, vibrational relaxation and reorientation of surrounding solvent molecules produce a thermalized intermediate. The free-energy change for exciplex formation is given by Eq. (15) (Fig. 7):

$$\Delta G_{EX} = E^0(D^+/D) - E^0(A/A^-) - \Delta G^* + \frac{e^2}{2} \times \left(\frac{1}{r_D} + \frac{1}{r_A}\right)\left(1 - \frac{1}{\varepsilon_s}\right) + E_{orb} - \frac{e^2}{d_{cc}} - \frac{\mu^2}{\varrho^3}\left(\frac{\varepsilon_s - 1}{2\varepsilon_s + 1}\right). \tag{15}$$

The exciplex or CIP is treated as a dipole of radius ϱ and dipole moment μ. The last term in Eq. (15) describes the energy of this dipole, based on the Kirkwood-Onsager model (assuming formation of a spherical complex) [14]. Thus, an exciplex or CIP is stabilized by Coulombic interactions and by solvation. The solvation energy is expected to be favored by increasing solvent polarity and a large dipole

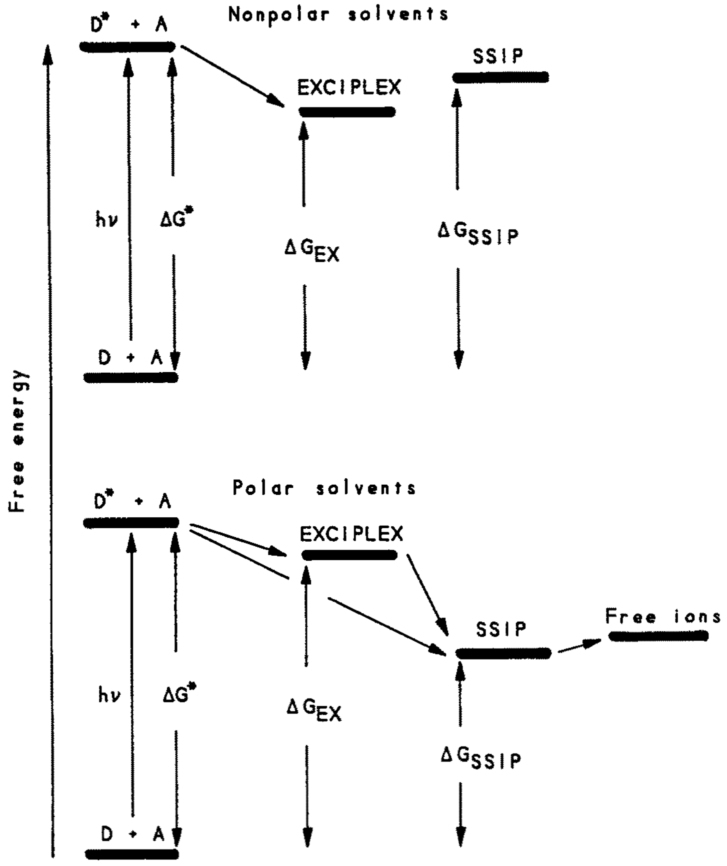
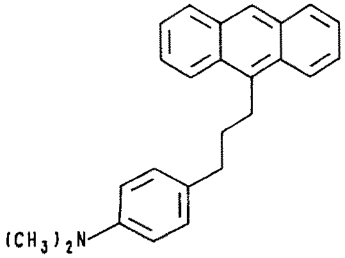


Fig. 7. The course of PET in solution depends on the polarity of the solvent. In nonpolar solvents, exciplexes are usually more stabilized than SSIP. In polar solvents, which can stabilize an SSIP and free ions, this figure shows two pathways leading to free ions. The exciplex in a polar solvent may be more appropriately regarded as a contact ion pair

moment. Dipole moments of exciplexes can be determined by measuring exciplex fluorescence emission at various solvent polarities [17]. E_{orb} is the difference between destabilizing and stabilizing orbital interactions ($E_{orb} = E_{dest} - E_{stab}$). Consequently, exciplex stabilization may also be enhanced by orbital interactions which favor E_{stab}.

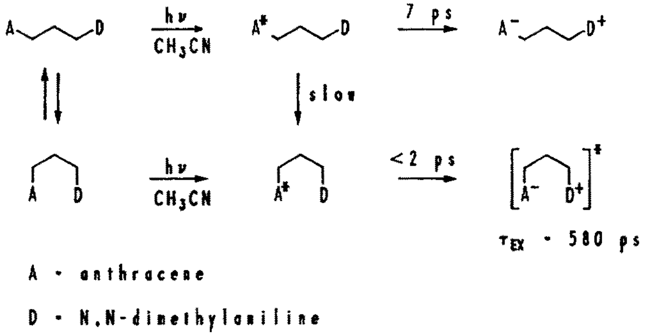
In polar solvents, the pathway to free ions may proceed from the encounter or collision complex through an exciplex (or CIP), in competition with direct formation via a SSIP (Fig. 7). The actual pathway is determined by the magnitudes of the Kirkwood-Onsager and Born energies, electrostatic effects, and orbital interactions. In polar solvents, the indirect pathway involving exciplex formation may be unfavorable because of a energy barrier due to a large ΔG_{sol}. If ion pairing takes place at all in polar solvents (as may occur if the Born term is equal to or less than the Kirkwood-Onsager term), the ions may dissociate into an SSIP and finally into free ions because polar solvent molecules may penetrate the space between ions of opposite charge and effectively weaken electrostatic attractions. As noted before, escape of the ions from the cage is more favorable in polar solvents.

Some exciplexes, however, can be stabilized in polar solvents because of favorable orbital interactions, electrostatic effects, or a Kirkwood-Onsager solvation energy term [18]. For example, in polar solvents an exciplex structure with a large dipole moment can be stable with respect to solvent-separated and free ions (Fig. 8). The lifetimes of these exciplexes should then be sufficiently long to allow for observation. In fact, there is evidence to support exciplex emission even in polar solvents. Eisenthal and coworkers, for example, observed the exciplex emission of 9-anthracene-$(CH_2)_3$-*N*,*N*-dimethylaniline systems in acetonitrile [19]:



(16)

On photoexcitation, the anthracene moiety is excited into a singlet state. Exciplex formation then proceeds probably via a folded conformation in competition with "complete" electron transfer in an extended conformation:



(17)

The observation of long wavelength emission in acetonitrile is evidence for exciplex formation. Davidson has also reported exciplex emission in polar solvents for a series of naphthalene-$(CH_2)_n$-*N*-alkylpyrroles (n = 0, 1, 2) exposed to 295 nm light [20]. In intramolecular systems, chain dynamics undoubtedly play a role in stabilizing intramolecular exciplexes in polar solvents [21], although there is little information concerning the structures of these exciplexes.

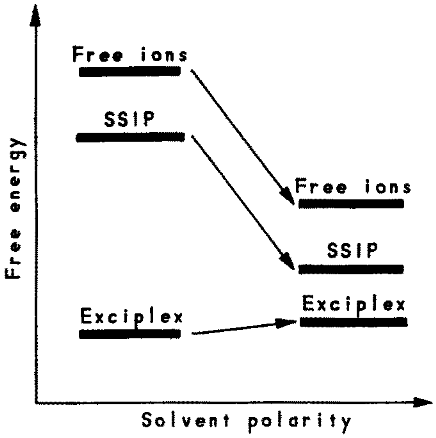


Fig. 8. Some exciplexes are stabilized even in polar solvents. See text for examples of systems where exciplex emission has been observed in polar solvents. These exciplexes may be stabilized because of favorable orbital interactions or enhanced solvation and Coulombic interactions

In nonpolar solvents, exciplex formation is usually favored because of a small ΔG_{sol} and a favorable Coulombic term. The ions are likely to remain in intimate contact for a longer time, i.e., ion pairing is effective because of favorable Coulombic and solvent effects. That dissociation into solvent-separated is not likely for exciplexes formed in nonpolar solvents has been shown by extensive studies dealing with the photochemical additions of donor and acceptors. Reactions via exciplexes or CIP's frequently yield cycloadducts, whereas in polar solvents, coupling via substitution of radical ion pairs and other chemical reactions involving solvated radical ions may predominate [12].

In medium polarity solvents, recent spectroscopic measurements have been able to distinguish between SSIP and CIP in studies on β-naphtholate [22]. This work confirms the general picture expounded by Winstein on the existence of various charge-transfer intermediates ranging from "tight" CIP's to "loose" SSIP's [23].

2.3 Spin Dynamics

During photoinduced electron transfer, spin-alignment is normally conserved, so that a singlet pair of reactants generates a geminate pair of doublet ions with overall singlet spin (Fig. 1). Similarly, PET between a triplet excited state and singlet ground state leads directly to a triplet pair of doublets. Singlet and triplet ion pairs are said to be spin correlated because of strong spin coupling. However, singlet and triplet ion pairs can interconvert via intersystem crossing, the S – T pathway being mediated by hyperfine coupling, the Zeeman splitting, and spin-orbital coupling (Fig. 9) [24]. Hyperfine coupling may play a major role in inducing an electronic spin flip when the energy separation or exchange interaction, 2J, between the singlet and triplet energy levels is smaller than the energy of hyperfine coupling, i.e., $2J < \Delta E_{hf}$. A spin flip can also be induced by the Zeeman interaction, which is due to the strength of an external magnetic field. The Zeeman interaction splits the T_+ and T_- sublevels away from T_0. This effect is proportional to the strength of the applied field. As the strength of the magnetic field is increased,

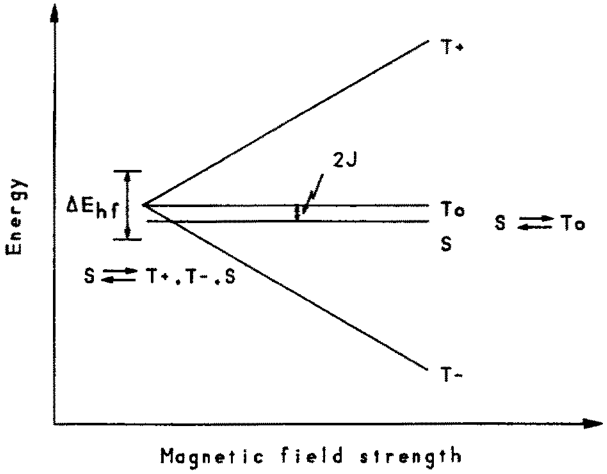


Fig. 9. The interconversions of the spin states of radical ions can be modulated by hyperfine coupling (ΔE_{hf}), the Zeeman effect, and spin-orbital coupling. When exchange interactions (J) are small, hyperfine coupling dominates in inducing singlet-triplet interconversions. J becomes very large at small distances separating the cation and anion radical, and at these small separation distances, spin-orbital coupling is important. The energy separations between the triplet substates (T_+, T_-, and T_0) can be increased by an external magnetic field. This phenomenon, the Zeeman effect, decreases $S \leftrightarrows T_+$ and $S \leftrightarrows T_-$ transitions, whereas the $S \leftrightarrows T_0$ is enhanced. Figure is redrawn from figures in Refs. [24, 25, 26, 27, 28]

the splitting of T_+ and T_- leads to fewer $S \rightarrow T_+$ and $S \rightarrow T_-$ transitions. The third mechanism, spin-orbital coupling, is usually operative when the exchange interaction between the radical ions is strong, i.e., $2J \gg \Delta E_{hf}$.

The singlet-triplet energy gap must be small for a spin flip to take place by hyperfine coupling [24]. However, because J decreases exponentially with the distance between the ions [25], J is negligible at large distances, and singlet-triplet splitting decreases, resulting in a maximum effect due to hyperfine coupling. On the other hand, J is large for contact ions and exciplexes, in which the singlet-triplet energy gap increases [26]. In these charge-transfer species, the effects of hyperfine coupling are cancelled, and intersystem crossing takes place predominantly by spin-orbital coupling.

With this background, it is of interest to consider intersystem crossing between singlet and triplet radical ion pairs in the presence of an external magnetic field in systems where the separation distance can be varied. Such an approach can lead to a differentiation between in-cage geminate from out-of-cage processes in certain donor-acceptor systems [26, 27]. To illustrate this point, we consider the work of Weller and coworkers, who undertook a series of extensive studies of magnetic effects on the PET of the pyrene-*N*,*N*-dimethylaniline system in acetonitrile [27]. Electron transfer between singlet pyrene and the amine quencher leads to a singlet ion pair and/or exciplex, which then recombines to ground-state reactants or triplet ion pair by intersystem crossing, in competition with escape from the solvent cage via ion dissociation. The escaped ions can diffuse back into the cage to form a singlet or triplet ion pair. Triplet pyrene, which can be monitored by its transient absorption, can be generated by recombination with the triplet ion pair:

$$\begin{array}{l} {}^1A^* + D \rightleftarrows {}^1({}^1A^* + D) \rightarrow {}^1({}^2A^- + {}^2D^+) \rightleftarrows {}^3({}^2A^- + {}^2D^+) \rightarrow {}^3A^* + D \\ \qquad \text{Recombination} \quad \swarrow \qquad\qquad \searrow \nwarrow \qquad \swarrow \nearrow \quad \text{Dissociation} \\ \qquad\qquad\qquad\qquad A + D \qquad {}^2A^- + {}^2D^+ \end{array} \tag{18}$$

A = aromatic hydrocarbon
D = aromatic amine.

The appearance of ${}^3A^*$ occurs within two time domains. A risetime in ~10 nanoseconds is due to rapid geminate recombination. However, a "slow" component appears within ~600 nanoseconds, due to the recombination of the dissociated radical ions. The "rapid" component is more sensitive to the external magnetic field, and the result is a decrease in yield of ${}^3A^*$. This observation suggests that within the radical ion pair, the two ions must separate slightly so that $\Delta E_{hf} > 2J$, to guarantee sufficient hyperfine coupling between degenerate S, T_+, T_-, and T_0 states to allow for formation of triplet pyrene. As the strength of the magnetic field increases, the Zeeman effect reduces the yield of ${}^3A^*$. There is an absence of a magnetic effect on recombination processes of dissociated ions since free ions separated by a large distance loose their coherent electron spin motion before reentry into the cage.

Weller [27, 28] and others [29] have extended these concepts to study the chain dynamics of pyrene connected by a polymethylene chain to *N,N*-dimethylaniline, A-$(CH_2)_n$-D. The dynamical motions of the polymethylene chain deliver the reactants to encounter distances where PET may occur. The chain may exist in an extended conformation (J_{min}) or most probable end-to-end conformation (J_{eff}). Weller has suggested that donor and acceptors linked by large chains behave somewhat like unlinked donor-acceptor pairs in a magnetic field, since the two ends of the chain can wrap around to allow the donor and acceptor to behave somewhat like diffusing molecules in solution (where $\Delta E_{hf} > 2J_{eff} > 2J_{min}$) [28]. With intermediate chains where $6 \leqq n \leqq 12$, the encounter distance is smaller resulting in an increase in J_{eff}, so that $2J_{eff} > \Delta E_{hf} > 2J_{min}$. Increasing the magnetic-field strength leads to degenerate S and T_- states, and the yield of ${}^3A^*$ reaches a maximum before dropping again. With small chains where $n \leqq 6$, $2J_{eff} > 2J_{min} > \Delta E_{hf}$, because of the close proximity of A and D. The effects of hyperfine coupling are cancelled by the increase in the S − T energy gap, and there is no discernible effect on the yield ${}^3A^*$ due to a change in magnetic-field strength.

As the preceding examples demonstrate, magnetic field effects can be useful in identifying the nature of charge-transfer intermediates in photoelectron transfer. In particular, with a better understanding of the relationships between ΔE_{hf} and J, and between J and the separation distance, we can predict that magnetic-field experiments, similar to those pioneered by Weller, will assist in differentiating exciplexes and CIP's from SSIP's.

3 Theories of Photoinduced Electron Transfer

The classical theories of Marcus and Hush have proven to be powerful frameworks for explaining the rate differences in electron transfers between ground-state metal complexes and between organic molecules in solution [30, 31]. In the 1970s, the Marcus-Hush theory was broadened to explain reactivity in PET [32]. In early models, the reactants were visualized as simple spheres reacting at contact distance; the environment was visualized as a homogeneous solvent.

Almost all classical models treat nuclear and electronic motion independently. Because the mass of an electron is so much smaller than the mass of a typical nucleus, the electron moves much faster. For all practical purposes the motion of a nucleus remains fixed during electronic motion. This is the premise on which the Born-Oppenheimer approximation is based, i.e., electronic motion can be treated separately from nuclear motion. To give the reader an appreciation of the time-scales involved, it is useful to note that "fast" electron motions can occur in the brief time of $\sim 10^{14}$ to $10^{16}\ \mathrm{s}^{-1}$, whereas "slow" nuclear motions take place from $\sim 10^{12}$ to $10^{13}\ \mathrm{s}^{-1}$. In the early 1950s, Libby used the Born-Oppenheimer approximation to explain the widely differing electron-transfer rates in certain transition metal complexes [33]. He hypothesized that in a simple electron transfer between two metal complexes, an electron is transferred, followed by a slower nuclear reorganization to compensate for the new electronic configuration of the

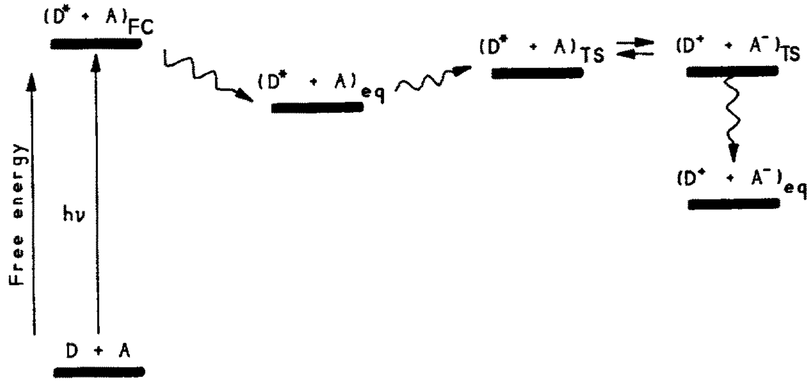


Fig. 10. Excitation of a donor (or acceptor) takes place as a vertical transition generating a Franck-Condon (FC) state with a different electron configuration but same nuclear geometry as the ground state. The Franck-Condon state undergoes equilibration to a thermalized excited state. In PET, the nuclei of the thermalized excited state (in this case, an electron donor), acceptor, and surrounding molecules undergo a reorganization to the geometry of the transition state. Electron transfer takes place rapidly within the transition state without any appreciable nuclear motion, generating a Franck-Condon-like radical ion pair. The "excited" radical ion pair subsequently undergoes equilibration to a thermalized ion pair

product state. This notion is fundamental to a qualitative and quantitative discription of photoelectron transfer. We visualize two molecular species, each consisting of a collection of electrons and a three-dimensional array of vibrating nuclei. One of these species is an electronic excited state. An electron then migrates rapidly between the excited state and ground-state species. The products formed by this electron transfer possess the nuclear configuration of the reactant state. A new nuclear array, corresponding to the new electronic configuration, is created. This description is similar to a transition during photoexcitation where a vertical electronic transition results in the Franck-Condon state which rapidly undergoes equilibration to a relatively long-lived excited-state.

On the basis of the Franck-Condon principle, photoelectron transfer between a donor and acceptor molecule proceeds as follows (Fig. 10). Initially, the donor and acceptor are dispersed randomly in a solution. On light absorption, the donor (or acceptor) undergoes a rapid transition to form a Franck-Condon state, which rapidly undergoes nuclear relaxation to an equilibrated state. A further nuclear reorganization takes place before electron transfer. After electron transfer, there is nuclear relaxation to the final, equilibrated product state.

Nuclear reorganization consists of changes in the internal or vibrational modes of the reactants as well as changes in the nuclear polarization of the surrounding solvent molecules. The distinction between these two classes of nuclear barriers is fundamental in understanding reactivity in photoelectron transfer. With this in mind, we shall now proceed to evaluate the barriers in electron transfer (Fig. 11). The classical theory, to be discussed in the next section, emphasizes the Coulombic and nuclear, whereas in the nonclassical, nonadiabatic theories, which are discussed in Sect. 3.3, emphasis is on electronic and nuclear barriers.

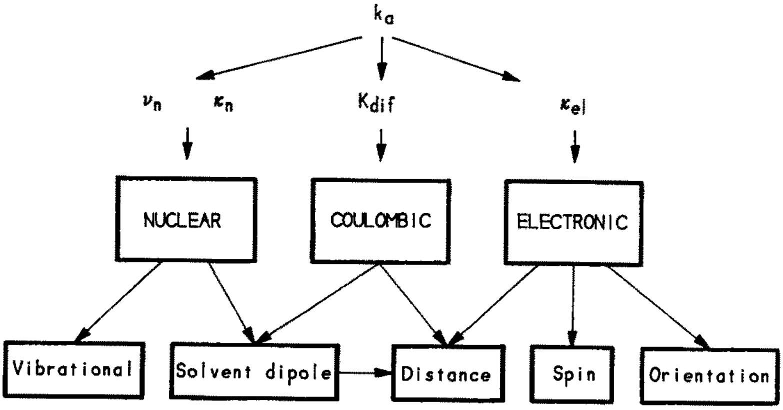


Fig. 11. Flow chart depicting the kinetic barriers in PET and the parameters which influence these barriers

3.1 Rate Expressions

In PET, an excited molecule and ground-state molecule are visualized as diffusing into an encounter complex and colliding a large number of times before reaction by electron transfer or diffusion from the cage. An operational format for this series of events is given Scheme 19 (where again, for simplicity, we assume that the excited molecule is an electron donor) [34]:

$$D^* + A \underset{k_{-dif}}{\overset{k_{dif}}{\rightleftarrows}} \underset{\text{Complex}}{\underset{\text{Encounter}}{D^* \ldots A}} \underset{k_{-el}}{\overset{k_{el}}{\rightleftarrows}} \underset{\text{Ion Pair}}{D^+ \ldots A^-} \xrightarrow{k_{ret}} D + A \qquad (19)$$

k_{dif} and k_{-dif} are diffusion rate constants; k_{el} is the unimolecular rate of electron transfer; k_{-el} is the rate constant for reversible electron transfer; and k_{ret} is the rate constant for return to ground-state reactants. To keep this analysis simple, the rate constants for ion dissociation, triplet recombination, chemical reactions, etc. have been omitted. A steady-steady treatment to the reactions in Scheme 19 then leads to

$$k_q = \frac{k_{dif}}{1 + \frac{k_{-dif}}{k_{el}}\left(1 + \frac{k_{-el}}{k_{ret}}\right)} \qquad (20)$$

where k_q is the bimolecular rate of quenching by electron transfer. If $k_{-el} \ll k_{el}$, i.e., the reaction is probably exothermic, Eq. (20) is simplified to:

$$k_q = \frac{k_{dif}}{1 + \frac{k_{-dif}}{k_{el}}} = \frac{k_{dif}k_{el}}{k_{el} + k_{-dif}}. \qquad (21)$$

With a further assumption, we can define two useful kinetic regions. If $k_{-dif} \gg k_{el}$, then $k_q = K_{dif}k_{el}$, where K_{dif} is the equilibrium constant for formation of the encounter complex, i.e., $K_{dif} = k_{dif}/k_{-dif}$. In this region, k_{el} values can be estimated from Stern-Volmer procedures, which measure k_q values. In the second region, $k_{-dif} \ll k_{el}$, and $k_q = K_{dif}$. In this case, the reaction is dominated by diffusion dynamics and is said to be diffusion-controlled.

The activated rate constant of electron transfer, k_a, is given by

$$k_a = K_{dif}k_{el}. \qquad (22)$$

Substitution of Eq. (22) into Eq. (21) leads to Eq. (23):

$$\frac{1}{k_q} = \frac{1}{k_{dif}} + \frac{1}{k_a}. \qquad (23)$$

For an electron transfer between two stationary molecules – perhaps those in the solid state or in an organized matrix – Eq. (24) can be written:

$$\frac{1}{k_q} = \frac{1}{k_a} \tag{24}$$

where k_a is a unimolecular rate constant.

With k_q values obtained by Stern-Volmer experiments, k_a can be calculated from Eqs. (23) or (24). For determining k_a in Eq. (23), k_{dif} can be estimated by various modifications of classical Smoluchowski theory [35] or by statistical nonequilibrium thermodynamic theory [36].

In the classical theory of Marcus, the rate determining factors involve nuclear reorganization. We write the first-order rate constant, k_{el} as [37]

$$k_{el} = \nu_n \kappa_n \kappa_{el} \tag{25}$$

where ν_n is the *nuclear frequency*. κ_n and κ_{el} are the *nuclear* and *electronic factors*, respectively. These dimensionless quantities, ranging from 0 to 1, are the probabilities that a specific electronic or nuclear barrier can be overcome. In the classical theory where two reactants collide to form the encounter complex, we assume that $\kappa_{el} = 1$ (conditions under which this assumption may not hold are considered in the next section). The complete expression for k_a then becomes

$$k_a = K_{dif} \nu_n \kappa_n \,. \tag{26}$$

We shall examine each parameter in Eq. (26), as each of these terms plays an important role in determining the overall rate of electron transfer.

The diffusion of the reactants to form the encounter complex (K_{dif}) may involve electrostatic barriers [38]. The following expression takes into account these Coulombic interactions [34]:

$$K_{dif} = \frac{4\pi N d^2 \delta d}{1000} \exp\left(-\frac{w_c}{RT}\right) \tag{27}$$

where $d + \delta d$ is the separation distance and the w_c is the Coulombic work required to bring the reactants within encounter distance. The expression for w_c is

$$w_c = \frac{z_D z_A e^2}{\varepsilon_s d[1 + 2.91(\mu/\varepsilon_s)^{1/2}]} \tag{28}$$

where z_D and z_A are the charges on D and A, and μ is the ionic strength of the medium. Tables 2 and 3 list values of K_{dif} and w_c under various conditions. Accordingly, w_c can be neglected for neutral organic reactants, whereas this work term may be important for electron transfer between centers possessing formal charges, as in the case of many metal complexes.

Table 2. Effect of w_c on K_{dif}[a]

w_c (eV)	K_{dif} (1 mol^{-1})
−0.22	1477
−0.09	9.7
−0.04	1.4
0	0.30
0.04	0.063
0.09	0.009
0.22	0.00006

[a] Calculated with Eq. (27) assuming that d = 7 Å, δd = 0.8 Å, and T = 300 K.

Table 3. Influence of separation distance and ε_s on w_c

$\varepsilon_s = 37$

	z_Dz_A						
	4	2	1	0	−1	−2	−4
d (Å)							
10	0.16	0.08	0.04	0	−0.04	−0.08	−0.16
9	0.17	0.09	0.04	0	−0.04	−0.09	−0.17
8	0.20	0.10	0.05	0	−0.05	−0.10	−0.20
7	0.22	0.11	0.06	0	−0.06	−0.11	−0.22
6	0.26	0.13	0.07	0	−0.07	−0.13	−0.26

$\varepsilon_s = 4$

	z_Dz_A						
	4	2	1	0	−1	−2	−4
d (Å)							
10	1.44	0.72	0.36	0	−0.36	−0.72	−1.44
9	1.60	0.80	0.40	0	−0.40	−0.80	−1.60
8	1.80	0.90	0.45	0	−0.45	−0.90	−1.80
7	2.06	1.03	0.52	0	−0.52	−1.03	−2.06
6	2.40	1.20	0.60	0	−0.60	−1.20	−2.40

[a] Calculated with Eq. (28); values of w_c listed in eV

After the reactants diffuse into the encounter complex, the next step is the actual formation of the transition state. It is standard practice to employ potential energy diagrams consisting of intersecting parabolic curves. The potential energies of the reactant (precursor) and product (successor) states are plotted *vs.* the combined nuclear reorganizational changes which precede and succeed electron transfer (Fig. 12). The crossing point is the transition state where the electron transfer occurs. The classical theories discussed in the following section provide the formalism for examining the nature of the transition state.

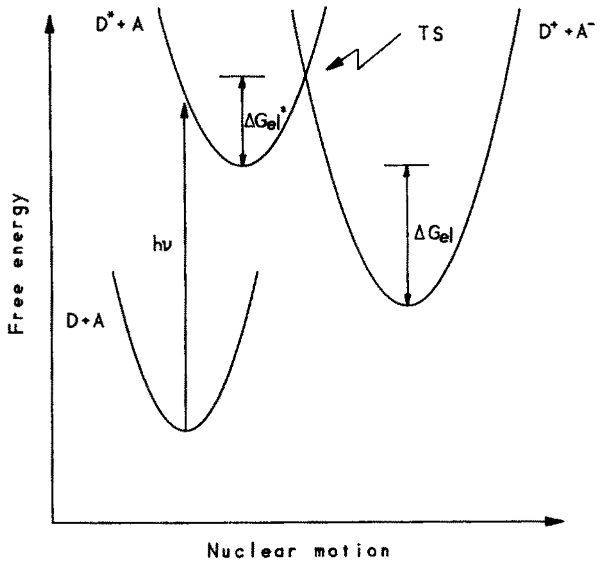


Fig. 12. PET can be studied on the basis of intersecting harmonic potential-energy curves. In the approach of Marcus, the free energy of a reacting system is represented as a function of nuclear geometry on the horizontal axis. During excitation, there is a vertical transition (Franck-Condon) to a point on the excited-state surface, followed by vibrational relaxation. Electron transfer takes place at the crossing of the excited-state and ionic potential-energy curves. The transition-state energy, $\Delta G_{el}^{\ddagger}$, corresponds to the energy difference between the minimum on the excited-state surface and the point of intersection

3.2 Classical Theories

In the classical Marcus-Hush theory, the initial nuclear geometry of the reactant state undergoes reorganization to the transition state prior to electron transfer [30, 31, 39]. The energy of the transition state, $\Delta G_{el}^{\ddagger}$, is gained by intermolecular collisions, in order to satisfy conservation of energy and momentum. The nuclear factor is related to the activation energy, i.e.,

$$\kappa_n = \exp\left(-\Delta G_{el}^{\ddagger}/RT\right) \tag{29}$$

where $\Delta G_{el}^{\ddagger}$ is

$$\Delta G_{el}^{\ddagger} = \frac{\lambda}{4}\left(\frac{\lambda + \Delta G_{el}}{\lambda}\right)^2 \tag{30}$$

and

$$\lambda = \lambda_v + \lambda_s . \tag{31}$$

λ is the total reorganizational energy; λ_v, the inner-sphere barrier, is the reorganizational energy due to vibrations within the reactants (v = vibrational); and λ_s, the outer-sphere barrier, is the reorganizational energy within the surrounding solvent molecules (s = solvent). ΔG_{el} is the free-change energy at the separation distance, d_{cc}.

λ is thus related to the entire nuclear reorganization of an electron-transfer reaction. These nuclear barriers, which precede the actual electron transfer, involve bond-length changes within the reactants, and reorientation of the surrounding solvent dipoles.

At the transition state, electron transfer takes place rapidly. During this brief moment, the nuclear geometry of the transition state remains fixed (the Franck-Condon principle). Following electron transfer, nuclear relaxation to the equilibrated successor state takes place. The products then separate from the successor state into the bulk of the solution. If the products are charged species, then the work, w'_c, involved as the ions separate is $w'_c = -w_c$, and can be estimated from Eq. (28).

Let us now take a closer examination of the expressions used to estimate the total reorganizational energy.

3.2.1 The Inner-Sphere Barrier

The reorganization energy due to bond-length changes, i.e., bond stretching, compression, bending, etc., can be estimated from

$$\lambda_v = \sum_j \left[\frac{f_i(R)_j\, f_i(P)_j}{f_i(R)_j + f_i(P)_j}\right] [\Delta q_i]^2 \tag{32}$$

where Δq_i is the difference in equilibrium bond distance between the reactant (R) and product (P) state corresponding to a jth vibration, and f_i is the force constant for this vibration. In practice, all vibrational states are assumed to display harmonic behavior, and the sum of all force constants and bond distortions of excited- and ground-state is taken in estimating λ_v [40]. In PET, estimation of λ_v requires a knowledge of bond-lengths and force constants in the reacting molecules before and after electron transfer. λ_v can be estimated for a variety of molecules to a first approximation. Table 4 lists representative values. The molecular parameters used

Table 4. Inner-sphere reorganizational energies

Reaction	λ_v (eV)	Ref.
$Fe(H_2O)_6^{2+} + Fe(H_2O)_6^{3+} \leftrightarrows Fe(H_2O)_6^{3+} + Fe(H_2O)_6^{2+}$	0.36	[39]
$Ru(NH_3)_6^{2+} + Ru(NH_3)_6^{3+} \leftrightarrows Ru(NH_3)_6^{3+} + Ru(NH_3)_6^{2+}$	0.03	[39]
$Ru(bpy)_3^{2+} + Ru(bpy)_3^{3+} \leftrightarrows Ru(bpy)_3^{3+} + Ru(bpy)_3^{2+}$	~0	[39]
N,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine ⇆ *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine + e^-	0.2	[42]
A-[Steroid]-Biphenylyl$^-$ ⇆ A$^-$-[Steroid]-Biphenylyl	0.45	[52]
1,1-diphenylethylene ⇆ 1,1-diphenylethylene cation + e^-	0.03	[43]

to estimate λ_v are available from a variety of sources. Bond lengths for transition metal complexes and organic amines can be estimated from X-ray crystallographic data. For greater accuracy, extended X-ray absorption fine structure (EXAFS) is used to obtain metal-ligand distances [41]. Hückel theory has been utilized to estimate Δq_i for excited- and ground-state aromatic hydrocarbons [42, 43]. Force constants can be calculated with empirical expressions [44]. Ab initio semiempirical molecular orbital theory employing the self-consistent field approach can yield more accurate force constants and bond lengths than conventional Hückel theory [45]. For example, the LCAO-SCF method has yielded accurate molecular parameters for radical ions and the singlet and triplet excited-states of certain conjugated hydrocarbons [46]. Alternatively, molecular mechanics programs can give respectable estimates of bond lengths. For example, the MMP2 program, an offshoot of the MM1 program introduced by Allinger [47], can be used for calculating the geometries of unconjugated systems. Nonetheless, one must proceed with caution in calculating λ_v, as there may be considerable deviations between theoretical and experimental values [48].

Electron transfers in which vibrational (bond) changes are predominantly rate determining are classified as "inner-sphere", i.e., $\lambda_v \gg \lambda_s$. These are to be distinguished from "outer-sphere" electron transfers where solvent motion plays the major role, i.e., $\lambda_s \gg \lambda_v$.

3.2.2 The Outer-Sphere Barrier

In PET, the rate can be markedly affected by the solvent polarity. With the formation of each new charge-transfer intermediate, solvent dipoles undergo reorientation in response to the new charge distribution on the reactants [49]. The solvent response influences the free-energy barrier of the reaction by altering the potential energy surface of the electron transfer. We consider this facet of solvent motion in this section. In a later section, we examine "dynamical" solvent effects.

λ_s measures the energy barrier involved as the solvent dipoles change. For spheroidal molecules, the following expression was first used by Marcus

$$\lambda_s = \Delta e^2 \left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{d}\right)\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s}\right) \tag{33}$$

where ε_∞ is the optical dielectric constant of the solvent (ε_∞ is equal to the square of the refractive index) [31]. According to Eq. (33), the solvent medium responds to changes in the charge distribution of the excited state and quencher during electron transfer. During formation of the transition state (Fig. 13), the surrounding solvent molecules undergo reorganization to adapt to the "nonequilibrium polarization" of the transition state. This reorientation corresponds to the slow motions of the solvent dipoles, and is related to ε_s. When electron transfer takes place within the transition state, the electron clouds of the solvent molecules respond immediately to the rapid fluctuation of electron charge. The "fast" component of the solvent polarization is associated with ε_∞.

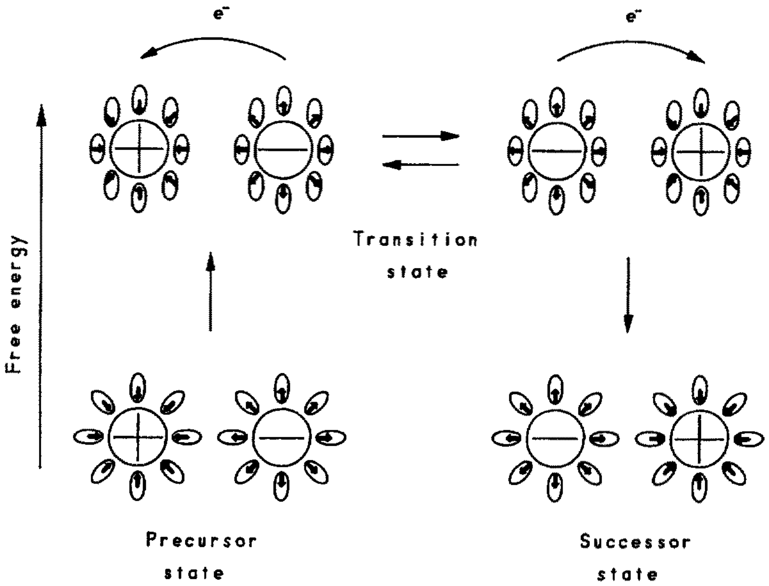


Fig. 13. A hypothetical representation of solvent molecule orientation in the transition state involving electron transfer between two charged reactants. Each solvent molecule possesses a permanent dipole, which in this idealized diagram is depicted by an ellipsoidal shape. Solvent molecules reorganize to the geometry of the transition state. The electronic polarization of the solvent molecules, represented here by the bold arrows, then responds practically instantaneously with electron transfer. Finally, the permanent dipoles of the solvent molecules readjust to the successor state. This model may not be applicable to electron transfer between neutral rectants (see text)

Equation (33) gives approximate estimates of λ_s for spherical reactants (Table 5). These values are undoubtedly overestimates [16, 50]. However, various attempts have been made to provide more realistic values. For example, in some models, the reactants are visualized as oblate ellipsoids, separated by a distance $d^{\ddagger}$ in the transition state [39]. Other models take into account the charge

Table 5. Outer-sphere reorganization energies[a]

r_D	r_A	Water	CH_3CN	Ethanol	Glycerol	Benzene
(Å)		(eV)				
2	2	1.98	1.90	1.79	1.57	0.02
4	2	1.65	1.58	1.50	1.31	0.01
6	2	1.65	1.58	1.50	1.31	0.01
4	4	0.99	0.95	0.90	0.78	0.01
6	4	0.86	0.82	0.78	0.68	0.01
6	6	0.66	0.63	0.60	0.52	0.01

[a] Calculated with Eq. (33); reactants are assumed to be spherical and in contact during the electron transfer

distribution of the reactants. In this connection, Suppan has raised a provocative question concerning the interpretation of λ_s in electron transfer between neutral reactants [16]. In Suppan's model, solvent reorganization preceding electron transfer is improbable. In fact, the solvent molecules surrounding the neutral reactants are arranged randomly. The ion pair is formed in an "unrelaxed" state and is eventually stabilized. The barrier in reaching the transition state is the "fast" polarization, and this barrier may be lowered in solvents having a high refractive index.

3.2.3 The Nuclear Preexponential Factor

The frequency of nuclear motions which take place as the precursor state adjusts to the transition state is related to ν_n. Typical values range from $\sim 10^{12}\,\mathrm{s}^{-1}$ for nuclear, intramolecular vibrations to $\sim 10^{14}\,\mathrm{s}^{-1}$ for reorientation of solvent dipoles. During the course of an electron transfer, the rate may be influenced by the response of the solvent polarity to changes in charge distribution on reactants. In the previous section, we considered the effects of solvent on $\Delta G^{\ddagger}_{el}$. However, there is also the dynamic effect of solvent motion, which is reflected in the preexponential factor, ν_n [49, 51]. In simple continuum theory, the polarization of solvent dipoles is given by the longitudinal relaxation time, τ_L, which is related to the dielectric properties of a solvent by $\tau_L = (\varepsilon_\infty/\varepsilon_s)$, where ε_∞ is the high frequency dielectric constant. For outer sphere adiabatic electron transfer (where $\kappa_{el} = 1$), the maximum rate is $k_{el} \propto \tau_L^{-1}$. In practice, $k_{el} \propto \tau_{obs}^{-1}$ where τ_{obs} is the observed relaxation time. There are many examples where the reactants and products are strongly coupled to dynamical solvent reorientation. One such system is the photoexcitation of (phenylamino)naphthalenesulfonate compounds leading to "twisted" fluorescent excited-states, [51].

3.2.4 The Inverted Region

Equation (30) predicts a parabolic relationship between the driving force and the activation energy in electron transfer. This relationship, one of the remarkable predictions of Marcus theory and one which runs counter to our intuition, suggests that the rate of electron transfer should decrease at large negative values of ΔG_{el}. Although experimental verification of the inverted region has been difficult to obtain, evidence has been obtained in rigid intramolecular systems where diffusion cannot "mask" the changes in k_{el} [52].

According to Eq. (30), the rate should maximize at $\Delta G_{el} \simeq -\lambda$; therefore, the onset of the inverted region should be related to the parameters which control λ. This fact can be exploited when it is desired to change the rate of an electron transfer by increasing λ [53]. The practical implications are discussed in a later section.

3.3 Nonadiabatic Theories

In the classical theory, the donor-acceptor orbitals were assumed to overlap slightly at a separation distance of ~7 Å within an encounter complex. However, there are many systems where the donor and acceptor are separated by greater distances. For example, in rigid environments or in intramolecular systems where the donor and acceptor are linked by a rigid or flexible molecular bridge, the separation distance may well exceed ~7 Å. In these systems, electronic as well as nuclear barriers may be rate limiting, and PET takes place by electron or nuclear tunneling through these energy barriers. A nonclassical treatment is required for these systems where emphasis is placed on the overlap of electronic and nuclear wavefunctions in the initial and final states, rather than on the transition state as in the classical theory. The donor, acceptor, and medium are perceived as a supermolecule undergoing high energy bond deformations and low energy solvent dipole orientations. PET may then be regarded as a radiationless transition between two potential-energy surfaces proceeding at a rate given by

$$k_{el} = \frac{2\pi}{\hbar} |H_{el}|^2 \, FC . \tag{34}$$

Equation (34) is the Fermi "Golden Rule" expression, where H_{el} is the electronic interaction, and FC is the Franck-Condon factor. The analytical version of Eq. (34), applicable to high temperature, is given by Eq. (35):

$$k_{el} = \frac{2\pi}{\hbar} |H_{el}|^2 \frac{\exp[-(\Delta G_{el} + \lambda)^2/4\lambda k_B T]}{(4\pi\lambda k_B T)^{1/2}} . \tag{35}$$

Equation (35) describes electron transfer in a "fixed-site" system. H_{el}, the electron matrix element, is identified with k_{el}, or the probability that the reaction proceeds from the initial to final state. Electron transfers can be regarded as taking place in adiabatic, nonadiabatic, or intermediate regions (Fig. 14), depending on the magnitude of H_{el}, which is related to the degree of orbital interactions between donor and acceptor [54]. In the adiabatic region, electronic interaction is strong, and therefore $\kappa_{el} = 1$. An example of an adiabatic reaction is the formation of exciplexes between planar aromatic molecules. In these systems, the orbital-electronic interaction between reactants is strong. At the other extreme, $\kappa_{el} = 0$, and the electron transfer is classified as nonadiabatic. The electron must tunnel through an energy barrier separating the donor and acceptor. Somewhere between the extremes lies an intermediate region which is called "weakly adiabatic", i.e., $0 < \kappa_{el} < 1$. This is the region applicable to classical theories where the donor and acceptor are assumed to approach to an approximate encounter distance of ~7 Å to allow for sufficient orbital interaction.

In nonadiabatic PET (where $\kappa_{el} = 0$), emphasis is placed on the effect of H_{el} on k_{el} (nuclear organization is not neglected, however). The magnitude of H_{el} is

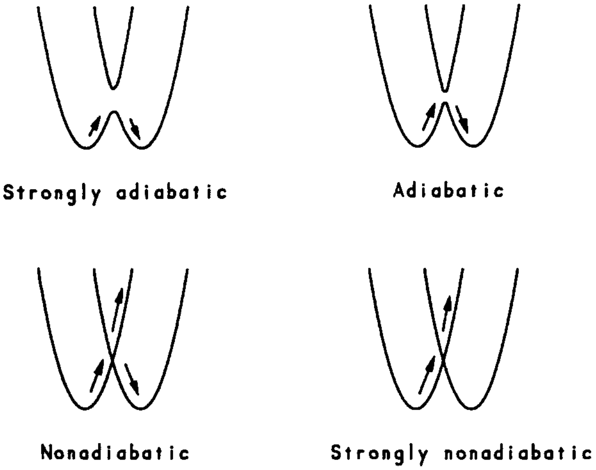


Fig. 14. The electronic transfer is strongly adiabatic if the orbital interactions are strong. This is the case when the separation distance is small or the orientation of the two reactants results in maximum orbital overlap. In contrast, if the separation distance is large, the electron transfer is nonadiabatic

affected by factors which influence the overlap of donor and acceptor orbitals, i.e., separation distance and orientation. It has been shown, for example, that H_{el} decreases exponentially with separation distance, i.e., $H_{el} = H^0 \exp(-\beta)$, where H^0 is the electronic interaction at contact distances, and β is an orbital parameter inversely proportional to orbital overlap. The rapid exponential decrease in H_{el} with separation distance has been demonstrated in many systems, one example

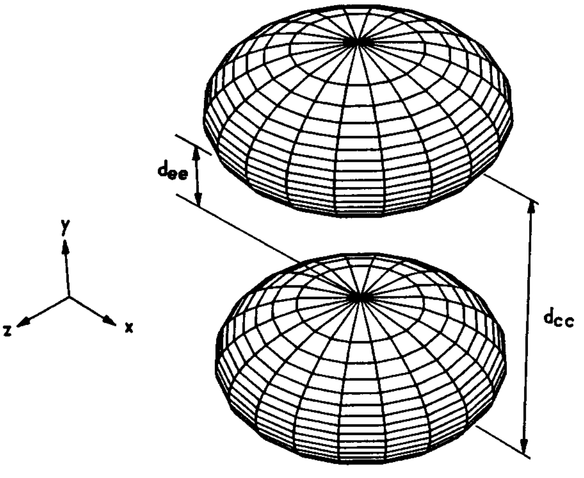


Fig. 15. The shapes of reactants in PET may be visualized as oblate spheroids. H_{el} is determined by the shapes and nodal characters of the interacting orbitals calculated for constant edge-to-edge and center-to-center distances. In this highly idealized drawing, the reactants approach in an face-to-face arrangement

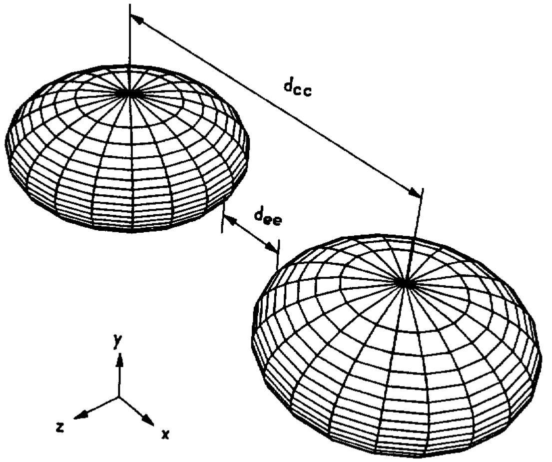


Fig. 16. Same as Fig. 15, but here the reactants are approaching in a end-to end orientation

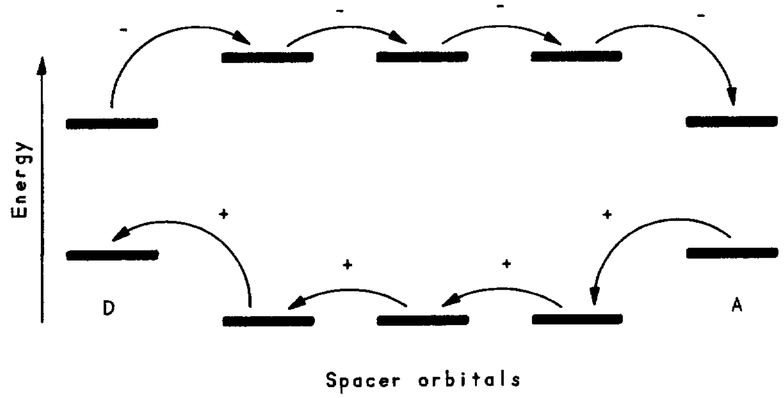


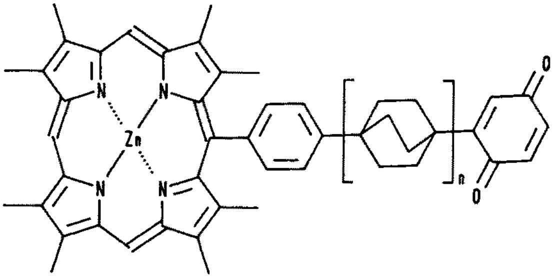
Fig. 17. According to some models discussed in text, PET in intramolecular rigid systems takes place by an electron hopping from the donor orbital along the LUMO of the spacer molecule or by "hole" hopping from the acceptor orbital along the HOMO or the spacer. These pathways are modulated by the energy gap between the orbitals of the spacer and those of the donor and acceptor

being the quenching of several homologues $[\mathrm{Ru(byp)}_3^{2+}]^*$ by methylviologen in rigid glycerol [55]. Using the Perrin "capture volume" model, it was deduced that the maximum separation distance does not exceed ~15 Å. This is the same separation distance predicted on the basis of the exponential dependence.

Detailed calculations on reactants visualized as oblate spheres have shown that H_{el} also depends on the shape and nodal character of overlapping orbitals [56]. Thus, H_{el} for planar π-conjugated systems is predicted to vary depending on the relative orientation of the molecules (Fig. 15 and 16). Orbital character has special importance in PET where overlap between orbitals of the quencher and the rapidly oscillating wavefunctions of the excited reactant determines the extent of electron coupling.

In this connection, it mus be mentioned that orbital interactions may occur via "through-space" or "through-bond" pathways [57]. In rigid intramolecular systems, for example, it is generally assumed that an electron may tunnel through the bonds of the molecular bridge separating the donor and acceptor. H_{el} then decreases exponentially with the number of bonds through which the electron tunnels. Figure 17 depicts two tunneling pathways. In the first, the electron travels from the donor to acceptor through the LUMO's of the molecular bridge. In the second pathway, the electron transfer occurs via a *hole* mechanism where a positive charge travels from the acceptor to donor via the HOMO's of the molecular bridge. The result is exactly as if an electron had been transferred from the donor to acceptor. These mechanisms depend on the coupling, or the energy gap, between the donor-acceptor orbitals and the orbitals of the molecular bridge.

An exceptional case of through-bond coupling where the distance dependence has been demonstrated is the electron transfer between singlet porphyrin and an electron-accepting quinone in a series of rigid porphyrin-bicyclo[2.2.2]octane-quinone systems [58]:



(36)

In this rigid system, the spacer keeps the donor and acceptor well apart (n = 1 – 2) and prevents overlap of porphyrin and quinone, so that electron transfer must take place through the bonds of the spacer.

According to Eqs. (30), (31), and (33), λ is predicted to vary with separation distance in distance-dependent nonadiabatic electron transfer. When the principal contribution to λ is related exclusively to solvent orientation, then $\lambda = \lambda_s$, and according to Eq. (30), $\Delta G_{el}^{\ddagger}$ should increase with increasing separation distance in the normal region ($-\Delta G_{el} < \lambda_s$), whereas in the inverted region ($-\Delta G_{el} > \lambda_s$), $\Delta G_{el}^{\ddagger}$ should decrease [59]. The distance dependence of λ_s must be interpreted in light of what model is selected to describe the transition state [59]. In dielectric continuum theory, the reactants are treated as simple spheres immersed in a uniform medium of constant dielectric, and the distance dependence of λ_s is a simple relationship. However, if the reactants are visualized within an ellipsoidal or spheroidal cavity, which itself is immersed in a dielectric continum, the distance dependence of λ_s should be less pronounced near contact distances where the reactants experience the nonpolar internal dielectric constant of the cavity. As the reactants separate and move closer to the edges of the cavity, the influence of ε_s in the solvent becomes more important.

Consequently, the relationship between k_{el} and distance may be complicated by a distance-dependent solvent barrier. Unless λ_s is very small, the variation in rate with increasing separation distance may be due to a change in solvent polarity. These considerations suggest caution in evaluating rate constants measured at varying distances and different solvents. Thus, the effects of distance on ΔG_{el} and λ_s should be evaluated separately. In the following section, we show how the distance and solvent dependence of ΔG_{el} and λ_s can be exploited to generate long-lived ion-pair intermediates.

4 Maximizing Ion-Pair Yields

In developing applications based on photoinduced transfer, one of the primary objectives of photochemists is to generate efficiently long-lived ion pairs. Not only must photoinduced charge separation be efficient but electron return as well as other product-forming and decay routes must not compete with "useful" chemical processes involving the ion-pair state. A "useful" process might be, for example, a photosensitized reaction to synthesize an organic molecule or the charge-separation required for efficient artificial photosynthesis. Unfortunately, the efficiency of these applications may be severely compromised in the presence of rapid rates of electron return. Consequently, photochemists have long been preoccupied with the challenge of generating long-lived ion-pair intermediates. Occasionally, the strategies employed have been imaginative. We will present only a brief overview here. A detailed discussion is presented in a later chapter.

Let us consider the pathways of PET in solution shown in Fig. 18. After formation of a geminate ion-pair, ion dissociation may take place in competition with reversible electron transfer, electron return, triplet recombination, and product-forming reactions. If we disregard product-forming steps and triplet recombination, the quantum yield, Φ_{ip}, for formation of free ions is [14, 60]:

$$\Phi_{ip} = \left(\frac{k_{eff}}{k_{eff} + k_{ret}}\right)\left(\frac{k_{dif}\tau_{es}[A]}{1 + \tau_{es}k_{dif}[A] + k_{-dif}/k_{el}}\right) \tag{37}$$

where

$$k_{eff} = \frac{k_{dis}k_{ret}}{k_{ret} + k_{-el}}. \tag{38}$$

In Eqs. (37) and (38), τ_{es} is the lifetime of the excited donor. k_{eff} is an "effective" rate constant for the formation of the ion-pair by reversible electron transfer. The first term on the right of Eq. (37) is the efficiency of ion-pair formation, defined here as $\alpha = k_{dis}/(k_{dis} + k_{ret})$ under the assumption that $k_{-el} \ll k_{dis}$. However, it should be noted that although k_{-el} is frequently neglected on the assumption that reversible electron transfer is too endergonic, there is evidence that at least in some systems reversible electron transfer can reduce the yield of free ions. For example, in the quenching of $[Ru(byp)_3^{2+}]^*$ and $[Ru(phen)_2(CN)_2]^*$ by organic

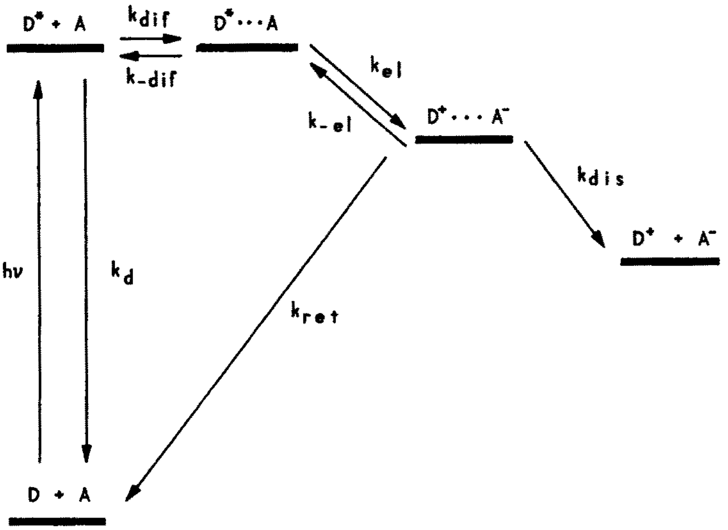


Fig. 18. Schematic diagram for charge separation and recombination in solution

donors and acceptors, kinetic studies suggest participation of reversible electron transfer and electron return [61]. In these reactions, k_{-el} and k_{ret} are influenced by electrostatic attraction and repulsion. When ions of opposite charge are generated in close proximity, i.e., $[Ru(byp)_3^{2+}]^* + A \rightarrow Ru(byp)_3^{3+} + A^-$, Coulombic attraction between the products tends to favor reversible electron transfer and electron return. On the other hand, when ions of the same charge are generated, they are likely to repel one another and dissociate, i.e., $[Ru(byp)_3^{2+}]^* + D \rightarrow Ru(byp)_3^+ + D^+$. The magnitude of k_{-el} is also influenced by the energy gap and entropic changes between the excited-state reactants and ion-pair.

Other studies have exploited medium effects to achieve the generation of long-lived intermediates. As pointed out earlier, choice of solvent can have a dramatic effect on the character of the charge-transfer intermediates. In exciplexes and contact ions, electron return usually takes place at the expense of ion dissociation, i.e., $k_{ret} \gg k_{dis}$. However, in more polar solvents, ion dissociation into free ions becomes energetically more favorable, and $k_{ret} \sim k_{dis}$.

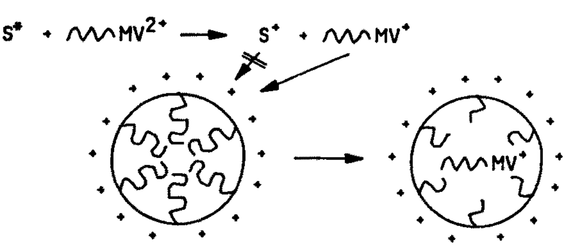


Fig. 19. A micelle can partition the positive sensitizer (S^+) from the viologen (MV^+) connected to a hydrocarbon chain, thereby preventing electron return. Such a system is very effective in maximizing the efficiency of charge separation (see text and Ref. [62]

A strategy shown in Fig. 19 uses the principle of "hydrophobic charge storage" [62]. In a solution of positively charged micelles, a water soluble sensitizer reduces a methylviologen linked to a hydrocarbon to a hydrophobic form. The reduced methylviologen rapidly enters the internal nonpolar environment of the micelle. At the same time, the positively charged sensitizer is electrostatically repelled by the positive surface of the micelle. Long-lived ion pair states result because of effective charge separation. Other studies have similarly exploited the concept of "partitioning" to control the outcome of photosynthesis by electron transfer [63].

Some investigators have noted a marked difference in Φ_{ip} based on the spin state of the ion pair. For example, Olmsted and Meyer have measured the efficiencies of ion yields for the quenching of a variety of excited organic and inorganic donors by methylviologen (MV^{2+}) as electron acceptor [64]. They found that for triplet ion pairs cage escape is more efficient than for singlet ion pairs. This observation can be explained on inspection of Fig. 1. With a triplet sensitizer such as anthracene derivative, cage escape is more efficient than for singlet ion pairs. However, electron return within the solvent cage to the ground state is spin forbidden for a triplet ion pair. Thus, there is an increase in the efficiency of ion dissociation. When the reaction is carried out in the presence of internal or external "heavy atoms", which may enhance spin-orbital coupling, triplet → singlet interconversion takes place to generate singlet ion pairs. Since electron return for the latter is spin-allowed, Φ_{ip} decreases. Similar considerations apply to the quenching of excited metal complexes because of large contributions of triplet spin character (the metal assists spin-orbital coupling). Working with carbonyl (triplet) and cyanoanthracene (singlet) excited states, Haselbach has also observed a variation in Φ_{ip} which can be explained in terms of the spin dynamics of the geminate ion pair [65].

The energy gap between the ion-pair and ground state can also control the rate of electron return, $k_{,et}$, and in effect influence Φ_{ip}. As noted earlier, the rate of electron transfer increases with an increase in the energy gap between an initial and final state until k_{el} reaches a maximum value, after which the rate begins to decrease again (the inverted region). This prediction can be used to control the

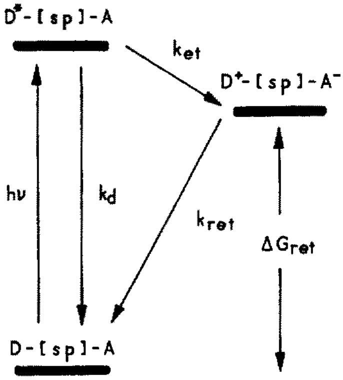
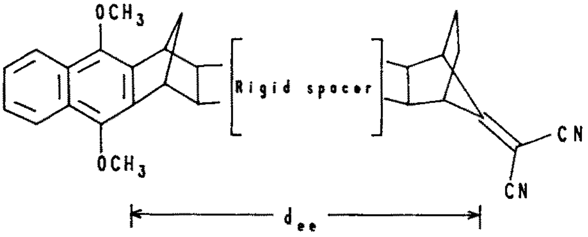


Fig. 20. Schematic diagram for charge separation and recombination for PET within a rigid molecular system

rate of electron return, k_{ret}, from the ion-pair state to ground-state reactants. For example, the magnitude of the energy gap between the ion-pair and ground state may fall within the energy range of the Marcus inverted region. In this case, k_{ret} may be much less than the rate constants for charge separation and there is consequently an increase in Φ_{ip}. Using ultrafast laser spectroscopy, Mataga has obtained values of k_{ret} for several number of organic donor-acceptor systems [66]. His results clearly demonstrate "inverted" behavior in electron return.

Similarly, a large energy gap between ion-pair and ground-state in intramolecular systems may result in enhancement in the lifetimes of the ion pair (Fig. 20). Thus, we note the trends observed for the "giant" dipoles in photoexcitation of methoxynaphthalene-[spacer]-dicyanoethylene compounds [67]:



d_{ee}, Å	k_{el}, s^{-1}	k_{ret}, s^{-1}
4.6	-	1×10^9
6.8	-	2×10^8
9.4	5×10^{10}	3×10^7
11.5	7×10^9	3×10^6
13.5	7×10^8	1×10^6

(39)

In this series of rigid molecules, the donor and acceptor are separated by an increasing number of saturated bridges. Singlet dimethoxynaphthalene donates an electron to dicyanoethylene. The formation of ion-pair intermediates, or "giant dipoles", was confirmed by transient microwave conductivity. The lifetime of each dipole state, given by $\tau_{ip} = 1/k_{ret}$, is increased because of the large energy gap for electron return. Further, values of k_{el} are much larger than k_{ret} because of the relatively small energy gap between the excited-state and ion-pair state, and also because of a small reorganizational barrier during the transition from the excited-state to ion-pair state. Because FC $\sim$ 1, the forward reaction is essentially "barrierless". However, the relatively smaller magnitudes of k_{ret} are probably due to the fact that $-\Delta G_{el} > \lambda$ (the inverted region).

In the previous example, it is important also to take note of the decrease in both k_{et} and k_{ret} with increasing separation distance. In devising artificial systems to mimic photosynthesis, chemists have exploited the distance dependence to maximize charge separation by synthesizing intramolecular models where the donor-acceptor distance is known. These models have proven to be useful in extending our understanding of electron transfer in biological systems, such as natural photosynthesis, in which a series of efficient charge separations takes place rapidly and efficiently because recombination electron transfers do not compete with each successive electron transfer [68].

The goal in many investigations has been to sort out the complex relationships among d, λ, and ΔG_{el} [69], with the aim of maximizing k_{el} and minimizing k_{ret}. It is hoped that this introduction will inspire the interested reader to assist in this effort. By unraveling this complex behavior, chemists will succeed in developing practical and novel applications based on PET.

5 Acknowledgements

The author wishes to express his appreciation to Professor Nicholas Turro of Columbia University for his interest and encouragement. The suggestions of Wen-Sheng Chung of Professor Turro's research group are also gratefully acknowledged.

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Photoinduced Electron Transfer (PET) Bond Cleavage Reactions

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Table of Contents

The primary objective of this chapter is to provide a review of the topic of photochemically stimulated electron transfer bond cleavage reactions for approximately the past ten years. PET stimulated bond cleavage reactions are an important way to initiate radical and/or

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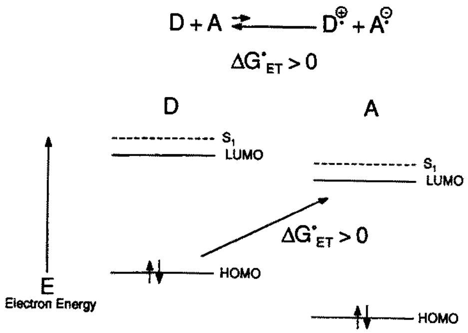
ionic chemistry that can be used in synthesis, imaging, photocuring, and photoresist chemistry. Several inter- and intramolecular photochemical single electron transfer (SET) induced bond cleavage reactions will be reviewed which result from either one-electron oxidation or one-electron reduction. A discussion of onium salt systems that undergo bond cleavage as a direct result of photochemical excitation of an electron from a π highest occupied molecular orbital (HOMO) to a σ* lowest unoccupied molecular orbital (LUMO) will also be provided. Examples of intramolecular rearrangement in, for example, aryldialkylsulfonium salts systems are also discussed. Although, most photochemical SET bond cleavage reactions occur in a stepwise manner through an ion-radical intermediate, if the initial substrate is uncharged, future trends in this field involve the use of concerted bond cleavage processes to eliminate energy wasting back electron transfer.

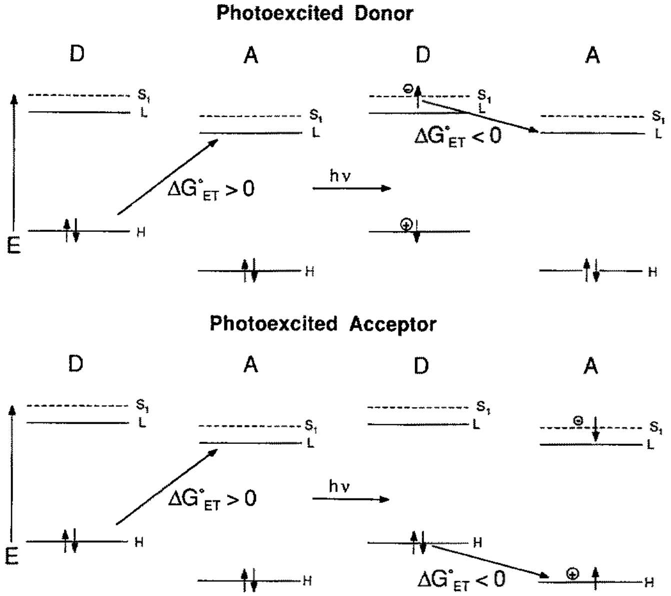
1 Introduction

The objective of this chapter is to provide a review of the topic of photochemically stimulated single electron transfer (PET) induced bond cleavage reactions for approximately the past ten years. This review, although not comprehensive, will cover intermolecular as well as intramolecular electron transfer (ET) bond cleavage processes from the point of view of the intermediates formed, e.g. ion-radicals/radicals, as well as the products obtained. An insight into the mechanistic aspects of PET bond cleavage reactions will also be provided. Although, most photochemical single electron transfer (SET) bond cleavage reactions occur in a step-wise fashion through an intermediate such as an ion-radical, concerted PET bond cleavage reactions will also be discussed.

The initial step of producing a photochemically excited state often provides the driving force for ET reactions that are not thermodynamically favorable when both electron donor and electron acceptor are in the ground electronic state. Both the electron withdrawing and accepting behavior of an electronically excited molecular species is enhanced by approximately the energy involved in the photoexcitation process. The electron accepting level for a molecule in the ground state, i.e., the lowest unoccupied molecular orbital (LUMO), is significantly modified when a molecule is in its excited singlet (S_1) or excited triplet (T_1) state. The energy of the LUMO level, which can be obtained from electrochemical reduction potential measurements, is usually at a different energy than the S_1 level due to electron exchange and coulomb interactions [1]. Michl and Thulstrup [1] have provided an excellent discussion of the relationship between the first excited singlet state, lowest excited triplet level and the LUMO level [1] in terms of these interactions. In this regard, Loutfy [2] and Saeva [3] have discussed the relative energies of the LUMO, S_1 and highest occupied molecular orbital (HOMO) in cyanine dyes and pyrylium salt systems, respectively. The energy of the HOMO level can be obtained from oxidation potential measurements and is specific for the solvent-reference electrode system used. Attempts to place the HOMO, LUMO and S_1 levels on an absolute energy level scale requires knowledge of the energy of the Fermi level for the reference electrode in a specific solvent system [2].

In view of the above, the photoexcited molecule can function as a powerful





one-electron reducing agent (electron donor, D) or a one-electron oxidizing agent (electron acceptor, A). The relative energies of the HOMO and LUMO levels for the situation when ET from D to A is highly endothermic, i.e., $\Delta G^0_{ET} > 0$, is shown above. However, when either D or A is electronically excited to the S_1 state, for example, the free energy change for ET from D to A becomes exothermic, i.e., $\Delta G^0_{ET} < 0$. The free energy change, ΔG^0_{ET}, for PET was first described by Weller [4] in the following relationship:

$$\Delta G^0_{ET} = E^{0'}_{red} - E^{0'}_{ox} - \Delta^1 E_{0,0} + C$$

where

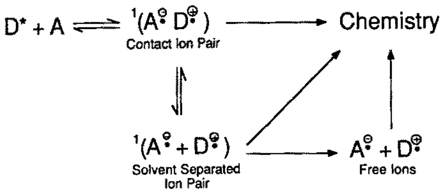
$E^{0'}_{ox}$ = oxidation potential of D,

$E^{0'}_{red}$ = reduction potential of A,

$\Delta^1 E_{0,0}$ = singlet energy or triplet energy ($\Delta^3 E_{0,0}$), and a Coulomb electrostatic term C.

Rates of ET have been correlated with ΔG^0_{ET}, a thermodynamic function, and found to increase as ΔG^0_{ET} becomes more exothermic until the Marcus inverted region is reached, when the rate of ET decreases with increasing exothermicity [5].

Once PET takes place then the ability or propensity of the intermediates, e.g. radicals or ion-radicals, to undergo chemistry such as bond cleavage depends on several kinetic factors. For example, the rate of bond cleavage must be competitive with the rate of deactivating processes such as back ET, and lifetimes of the singlet contact ion pair and solvent separated ion pair. Attempts have been made to



identify the specific radical ion-pair intermediate involved in photochemical reactions using the exciplex fluorescence quenching technique developed by Caldwell and Creed [6].

A discussion of oxidative PET bond cleavage reactions for several D systems will be presented in the following section.

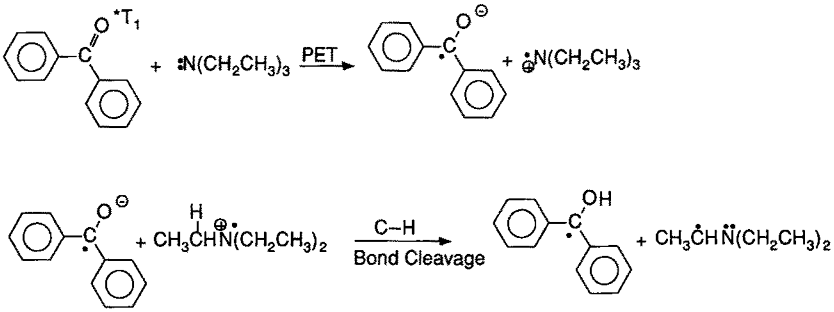
2 Oxidative PET Bond Cleavages

The chemistry of reactive species formed from one-electron oxidation of amines, borate salts, group 4a organometallics, bibenzyls, arenes and olefins will be treated separately in this section.

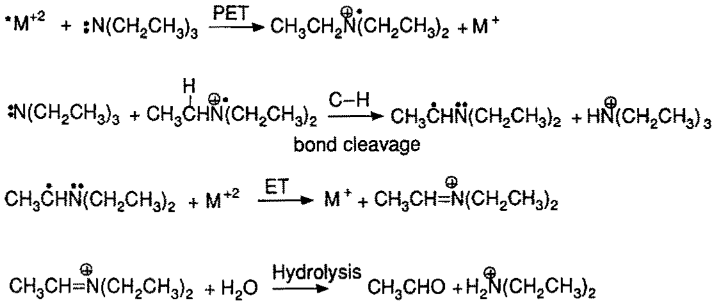
2.1 Amines

Aryl and aliphatic amines are perhaps the best known D molecules primarily due to the availability of the nonbonded electrons on nitrogen for PET processes. The simplest bond cleavage reaction for amine cation-radicals is heterolytic C−H cleavage or deprotonation. It is well known that the acidity of protons on a species after loss of an electron, i.e., after one-electron oxidation, is greatly enhanced [7]. For example, the pK_a of the benzylic protons in the toluene cation-radical have been estimated to be −10 [7] compared to pK_a value of ~35 before oxidation. The process of proton loss can be extremely fast, on the time scale of picoseconds [8].

Cohen and Guttenplan were the first to recognize that the photoreduction of triplet benzophenone by amines occurs via PET followed by proton transfer to



yield a radical pair [9]. More recently, Whitten and coworkers have described the photoreduction of polypyridyl complexes of ruthenium (II) and iron (II) by triethylamine (TEA) [10]. The TEA undergoes a series of chemical transformations initiated by PET and C–H bond cleavage as shown below. Deprotonation of the cation-radical species requires an external base such as TEA. Due to stabilization of the nitrogen cation-radical by an aromatic ring and heteroatoms aryldialkylamines would be expected to undergo a sequence of steps similar to TEA albeit at a slower rate.



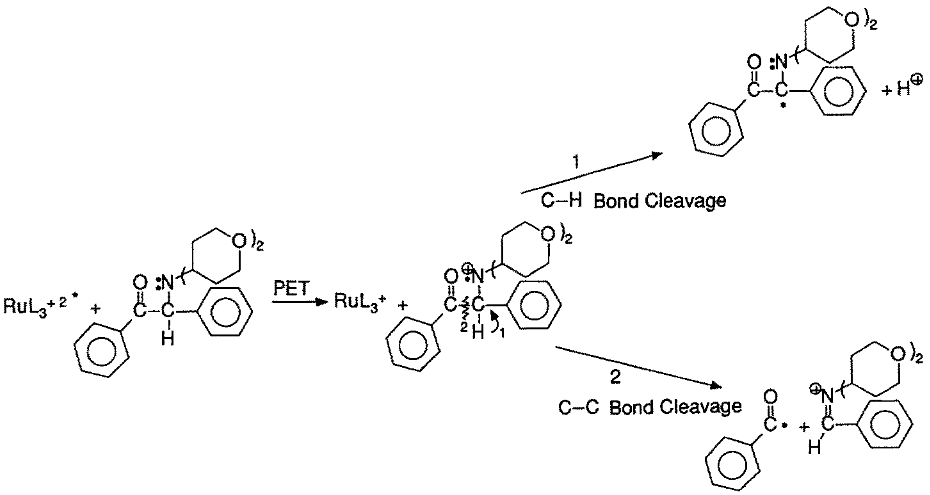
$$\cdot M^{+2} + :N(CH_2CH_3)_3 \xrightarrow{PET} CH_3CH_2\overset{\oplus\bullet}{N}(CH_2CH_3)_2 + M^+$$

$$:N(CH_2CH_3)_3 + CH_3\overset{H}{C}H\overset{\oplus\bullet}{N}(CH_2CH_3)_2 \xrightarrow[\text{bond cleavage}]{C-H} CH_3\dot{C}H\ddot{N}(CH_2CH_3)_2 + H\overset{\oplus}{N}(CH_2CH_3)_3$$

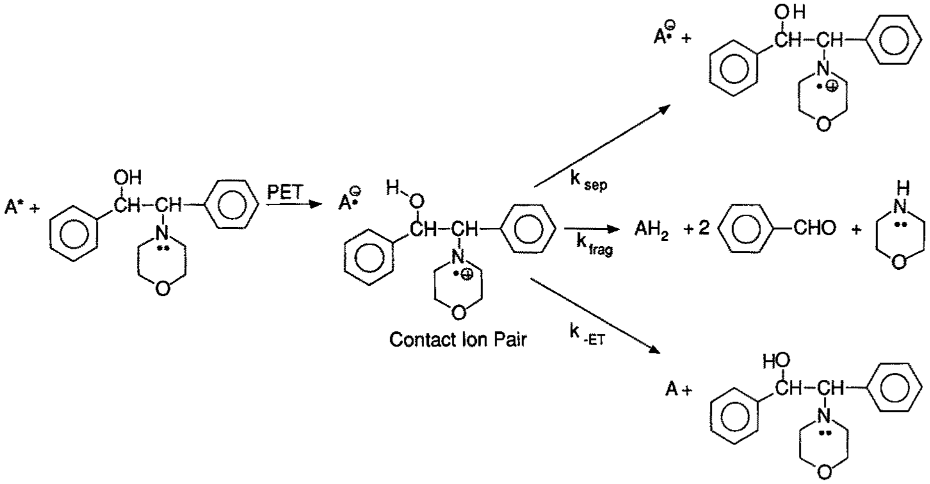
$$CH_3\dot{C}H\ddot{N}(CH_2CH_3)_2 + M^{+2} \xrightarrow{ET} M^+ + CH_3CH{=}\overset{\oplus}{N}(CH_2CH_3)_2$$

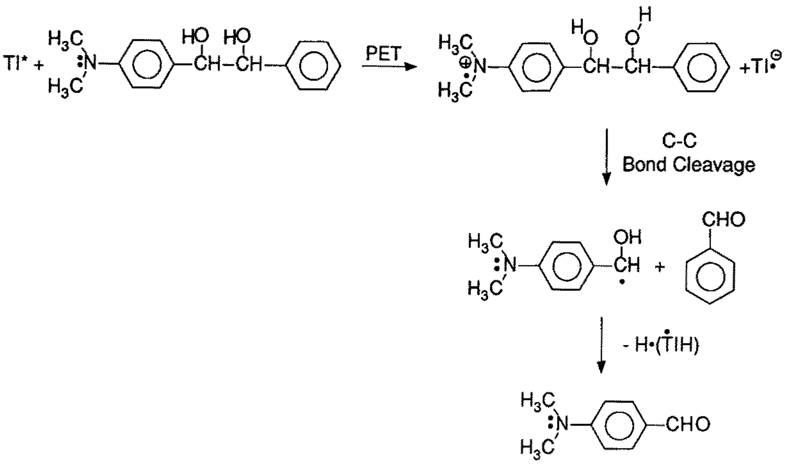
$$CH_3CH{=}\overset{\oplus}{N}(CH_2CH_3)_2 + H_2O \xrightarrow{Hydrolysis} CH_3CHO + H_2\overset{\oplus}{N}(CH_2CH_3)_2$$

Tertiary amines are frequently used as electron donors in photoreductions [11–15]. Depending on the structure of the tertiary amine C–C as well as C–H PET bond cleavage have been observed [14]. Using a ruthenium complex (RuL_3^{+2}) as the photoexcited A Whitten [14] has observed that nitrogen analogues of benzoin ethers undergo both C–H and C–C cleavage pathways via the amine cation-radical as shown.



Photochemical dehydrofragmentation has also been observed by Whitten et al. [16, 17] in PET reactions of aminoalcohols. The reaction is restricted to the geminate pair and the complimentary roles of reduced acceptor and oxidized donor facilitate chemical reaction in competition with back ET. The rapid fragmentation is dependent on the acceptor anion-radical induced deprotonation of the donor cation radical in the contact ion-pair and is strongly dependent on the structure of A [16]. The chemical transformation converts the aminoalcohol into the free amine, aldehyde and reduced electron acceptor. The efficiency of the PET induced fragmentation is affected by the stereochemistry of the aminoalcohol as well as the solvent [18]. Both the thioindigo (TI) and dicyanoanthracene (DCA) sensitized reactions are more efficient in nonpolar solvents such as benzene and

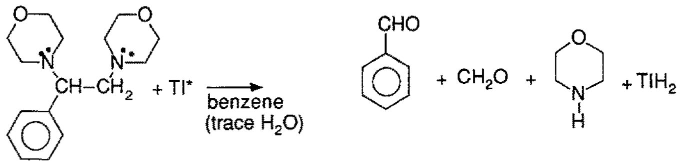


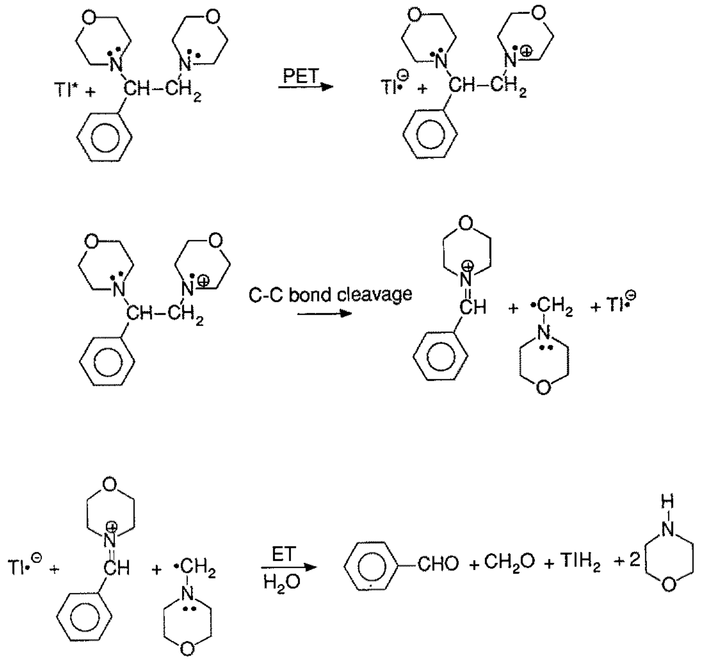


methylene chloride than in the more polar acetonitrile [16] presumably due to the enhanced basicity of the anion-radical in nonpolar solvents.

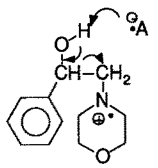
Other aminoalcohol systems [19] have been observed to undergo PET C−C bond fragmentation similar to "two electron Grob fragmentations" [20]. The isomeric α- and β-p-dimethylaminodesoxybenzoin and an aminodiol can be photooxidized by TI* to produce the corresponding cation-radical. Deprotonation by TI$^{\cdot-}$ leads to C−C fragmentation to form benzaldehyde and a benzyl radical stabilized by oxygen and a dimethylaminophenyl moiety. Hydrogen atom or electron and proton loss produces dimethylaminobenzaldehyde. The regioisomeric p-dimethylaminodesoxybenzoin derivatives undergo a similar C−C fragmentation to produce aldehyde and dimer products depending on the position of the hydroxy group [19].

Whitten and Kellett [21] have also investigated the PET C−C bond cleavage reactions of diamines using TI as the photooxidant. A general mechanism was proposed in which photoexcited TI produces the cation-radical of the diamine by SET [21]. Fragmentation of the C−C σ bond in the cation-radical is assisted by the unoxidized electron lone pair on the second nitrogen heteroatom center. If





the only temperature dependent process is the fragmentation process then an activation energy for the cleavage process is 3.9 kcal/mole [21]. The diamine fragmentation reaction was found to be insensitive to the acceptor anion-radical basicity in contrast to the aminoalcohols which require deprotonation to active C – C bond cleavage. The photofragmentation reactions of the diamine and

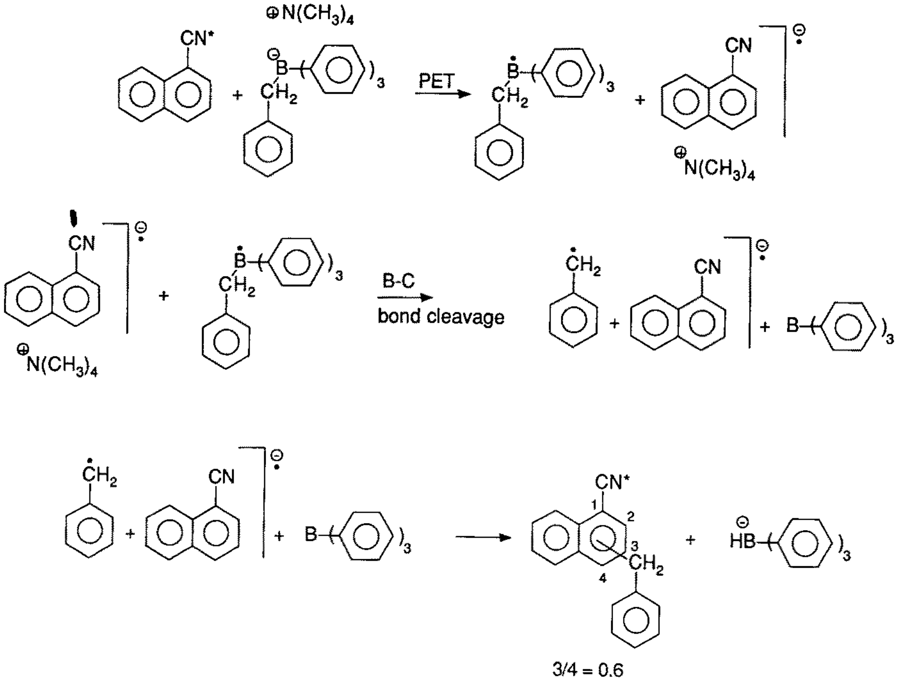


aminoalcohol were found also to be initiated by singlet oxygen as the excited acceptor [22].

An excellent review of PET bond cleavage reactions of amines has been recently published by Whitten and Ci [23].

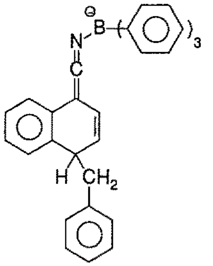
2.2 Borates

Alkyltriphenylborates have been observed by Schuster [24] to undergo B – C bond cleavage after PET. Irradiation of a cyanoaromatic electron acceptor, e.g. cyanonaphthalene, in the presence of tetramethylammonium benzyltriphenylbo-

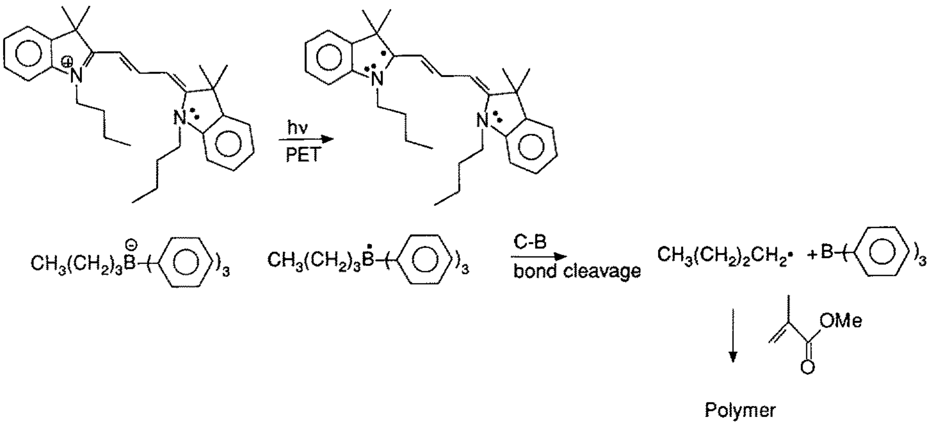


rate produces benzyl substituted cyanoaromates. The fluorescence of the cyanoaromatic electron acceptor is quenched by PET from the electron rich borate to the cyanoaromatic photoexcited singlet state producing a boron centered radical/anion-radical pair as shown.

The boron-centered radical undergoes a rapid B—C bond cleavage to produce a benzyl radical/cyanoaromatic anion-radical pair which combines to produce 3- and 4-benzyl substituted 1-cyanonaphthalenes in 95% yield. The authors suggest that the final substitution product is formed through a ketiminoborate intermediate. When 1,4-dicyanonaphthalene was used as the electron acceptor 3- and 4-substituted 1-cyanonaphthalenes are produced through an intermediate ketiminoborate which eliminates HCN when protonated.



More recently, Schuster [25] has demonstrated that cyanine dyes, i.e., cyanine borates or cyanine dye-borate mixtures, provide visible light activated initiation of free radical polymerization [26]. The photoexcited cyanine dye oxidizes alkyltriphenylborates by PET to produce the bleached reduced cyanine along with an alkyl radical. The alkyl radical can then initiate free radical polymerization [27]. This visible light activated PET bond cleavage is of considerable importance in photoimaging and photocuring [28].



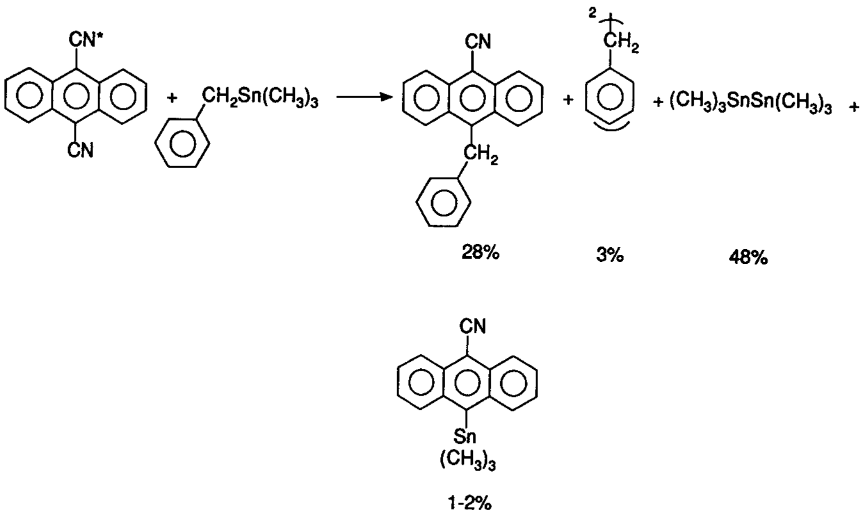
PET bond cleavage processes in group 4a organometallic compounds will be discussed in the next section. These processes are also important in photoimaging and photocuring [28].

2.3 Group 4a Organometallics

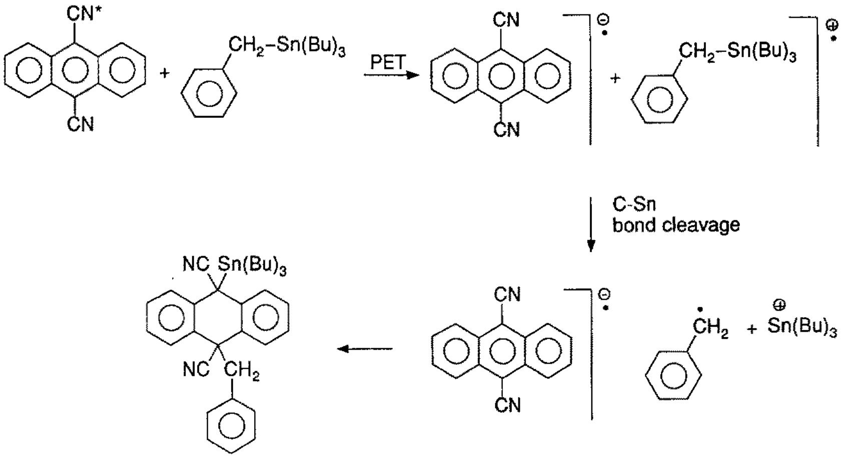
In 1974 Schweig [29] reported that one-electron oxidation of an organotin compound such as benzyltrimethylstannane is followed by cleavage of the intermediate cation-radical to produce benzyl radical and a tin-centered cation. Two years later Kochi and Gardner [30] observed charge transfer (CT) bands in the absorption spectra of several tetra-alkyl lead and tin compounds in the presence of tetracyanoethylene (TCNE) [30]. A correlation between the CT band energy and the ionization potential of the alkyl metals [30] was observed. Loss of CT absorption accompanied insertion of TCNE into the electron rich alkyl metal bond [30]. It was concluded that the chemical bond insertion reactions result from a thermally induced ET bond cleavage process [31–33]. Subsequently, Eaton has demonstrated that there is a dual pathway for oxidative cleavage of benzyltrimethylstannane providing both radical and cation products [33].

Eaton [34] was the first to utilize group 4a organometallics in PET bond cleavage reactions by using a weaker electron accepting component then TCNE to effectively turn off thermal ET. This photochemistry has clear application in unconventional imaging systems [27, 33–37].

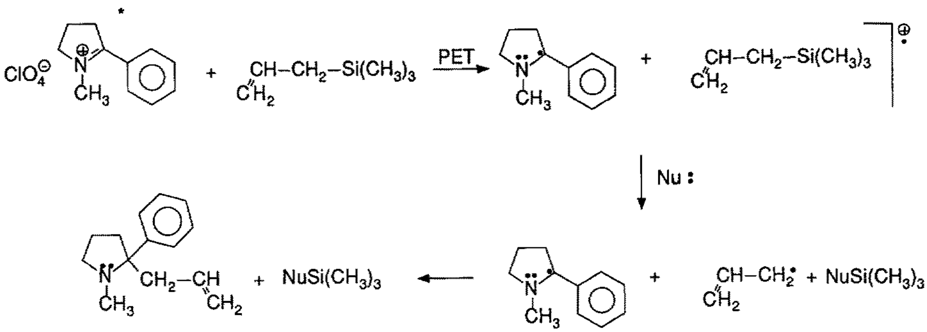
Benzyltrialkylstannanes, for example, quench the fluorescent photoexcited singlet state of 9,10-dicyanoanthracene (DCA) by PET from the stannane to the DCA [35]. Eaton has proposed that the observed products arise from secondary photolysis of an initial adduct between DCA and benzyltrimethylstannane through



a nonemitting charge-stabilized exciplex [35]. In mechanistic terms the photoexcited DCA abstracts an electron from the stannane to produce an anion-radical/cation-radical pair. The tin-centered cation-radical undergoes a C—Sn bond cleavage to provide benzyl radical and tributyl tin cation which add to the DCA$^{\cdot-}$. The benzyl radical produced can be used as an initiator for the free radical polymerization of acrylates and vinyl monomers [27].

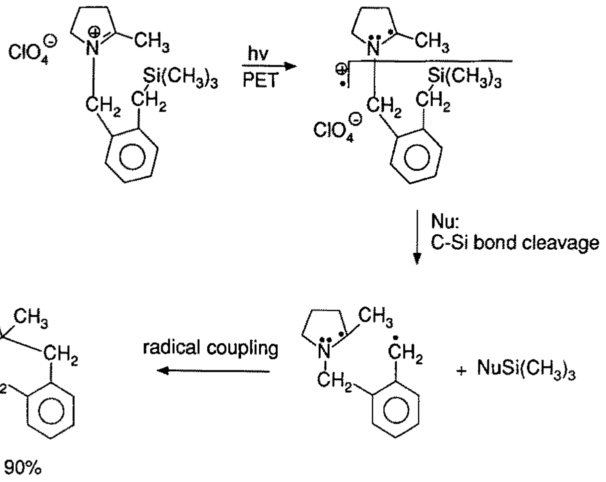


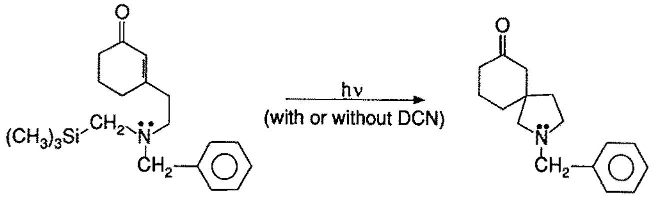
In an attempt to investigate the synthetic potential of PET bond cleavage reactions Mariano has explored the PET bond cleavage reactions of allylsilanes using electron deficient iminium salts as the photooxidant [36]. Allyltrimethylsilane is an efficient quencher of the fluorescent iminium salt excited singlet state with a rate near diffusion control [36]. The photoexcited iminium salt can oxidize the allylsilane moiety to provide a radical/cation-radical pair. The silane cation-radical undergoes a rapid Si—C bond cleavage presumably with assistance by nucleophilic attack on silicon by solvent or other nucleophilic species. This process

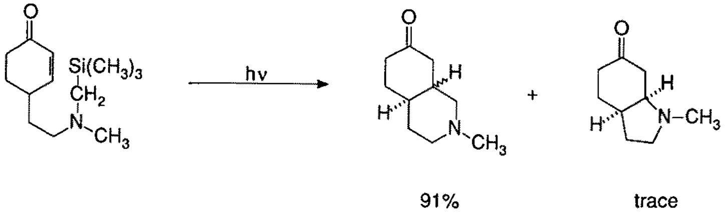


provides an allyl radical which couples with the iminium radical to form an allyl amine. Allylstannanes [37] and benzylsilanes were found to behave similarly [37].

Mariano and coworkers have exploited this PET bond cleavage chemistry in intramolecular as well as intermolecular cyclization reactions [38]. The combined iminium-benzylsilane functionalities undergo intramolecular PET to provide an intramolecular amine radical/benzyl silane cation-radical pair by exciting either the iminium salt or the arene chromophore [38]. Cleavage of the benzyl C–Si bond presumably takes place with assistance of moderately weak nucleophiles such as methanol. The diradical couples intramolecularly to provide an indolizidine derivative [38] in 90% yield.





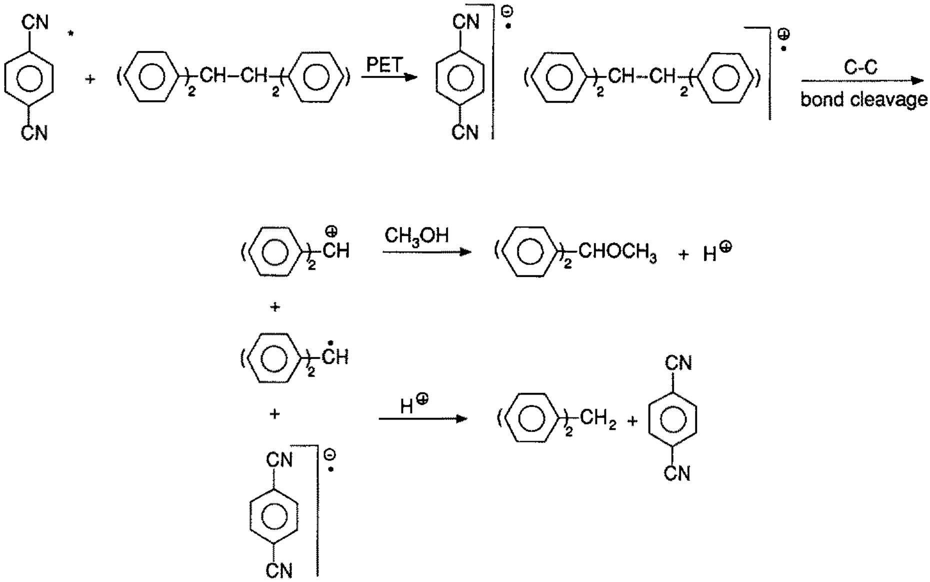


Intramolecular cyclization reactions have been observed which involve coupled aminosilanes and conjugated cyclohexenones to provide spiro and bicyclic *N*-heterocyclic compounds. The reaction can also be DCA sensitized [39].

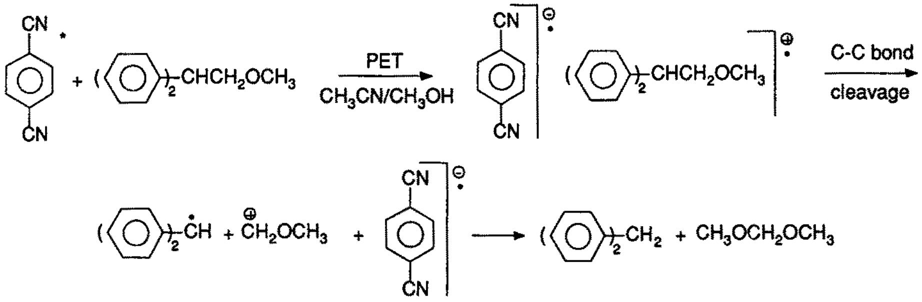
Benzyl and allyl radicals can also be formed from the corresponding hydrocarbon cation-radical by deprotonation or by C—C bond cleavage of the bibenzyl cation-radical. This topic will be discussed in the following section.

2.4 Bibenzyls, Arenes and Olefins

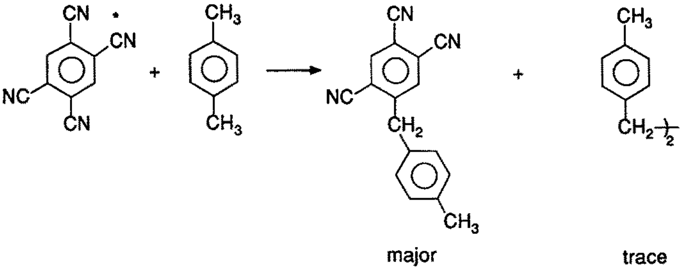
One-electron oxidation of an olefin, arene, or a bibenzyl group can lead to C—H or C—C bond cleavage to produce an allyl or benzyl radical [40, 41]. This area has been pioneered by Arnold [41]. The PET reaction of 1,1,2,2-tetraphenylethane and methyl-3,3-diphenylethyl ether have been reported by Arnold and coworkers [41] to provide heterolytic C—C bond cleavage through an intermediate tetraphenylethane cation-radical. The cation-radical intermediate fragments to diphenylmethyl radical and diphenylmethyl carbocation.

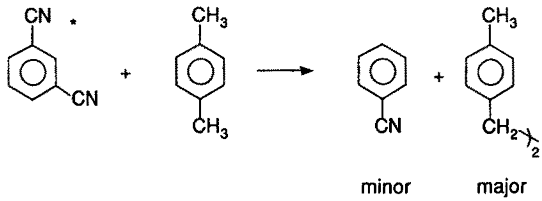


In general, the electron donor substrate is oxidized by PET to a cation-radical which undergoes C—C bond cleavage to form the most stable radical and cation pair. These species react further with solvent and with the reduced A to form hydrocarbon and ether products [41]. Griffin [42], Albini [43a], and Kochi [43b] have also contributed significantly to this research area.

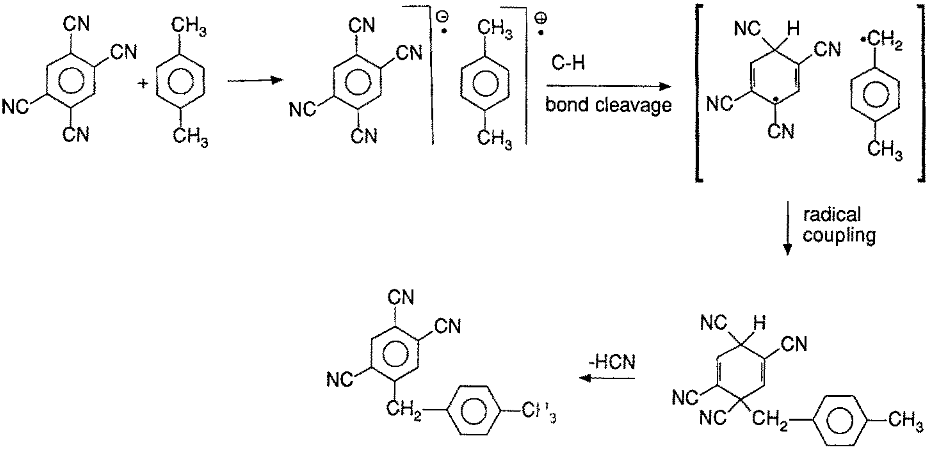


Lewis and Petisce [44] have investigated PET reactions between a number of cyano aromatic electron acceptors and electron donating methyl aromatic systems. Both substitution as well as dimer products have been observed depending on the electron affinity of the acceptor [44, 45]. When weak electron acceptors, e.g. *m*-dicyanobenzene and benzonitrile, were used dibenzyl derivatives were formed predominantly. In contrast, strong electron acceptors produced predominantly substitution products. For example, use of tetracyanobenzene with *p*-xylene produced predominantly in-cage substitution product while use of *m*-dicyanobenzene produced mainly out-of-cage coupling to form the bibenzyl derivative. Mechanistically the photoexcited electron acceptor oxidizes *p*-xylene to form a contact anion-radical/cation-radical pair which undergoes a C—H bond cleavage to produce a free radical pair. In-cage coupling of radicals produces photosubstitution after the loss of HCN. An out-of-cage reaction results in bibenzyl formation. The variation in the product distribution with A has been attributed to a difference in charge transfer character exhibited by the radical pair [44].

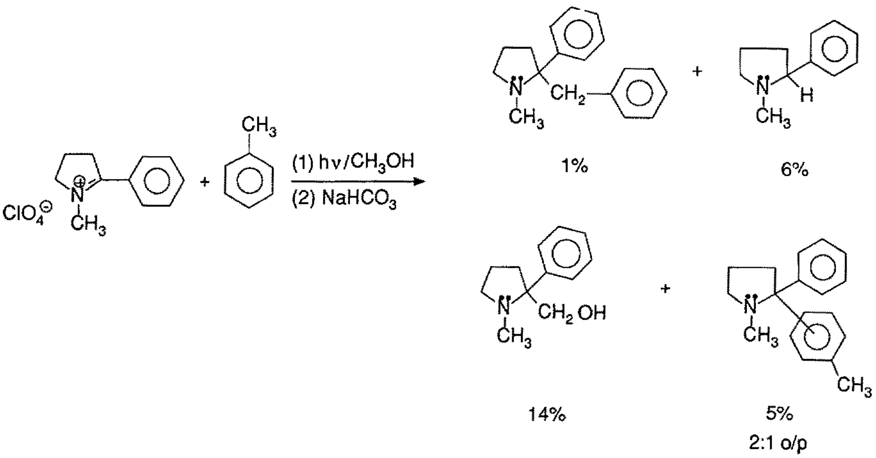




Mariano [46] has investigated arene-iminium salt PET photochemistry where the photoexcited electron accepting iminium salt has been used to oxidize toluene



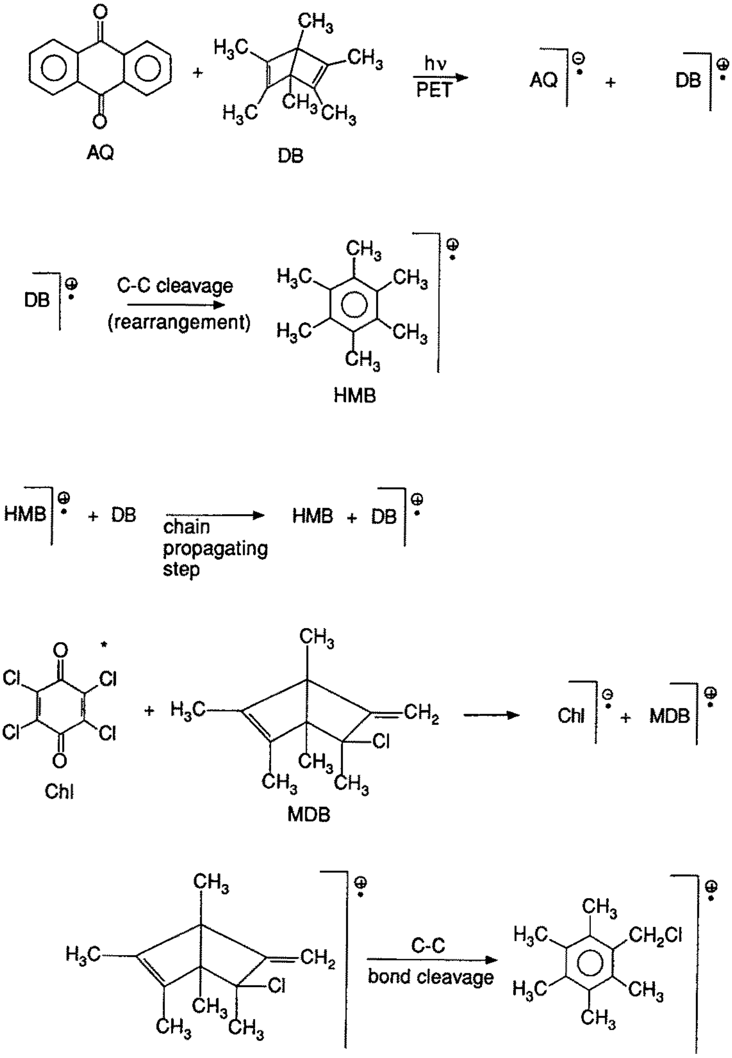
in methanol solvent. PET from toluene to the photoexcited iminium salt produces a toluene cation-radical/iminium radical pair which is presumably deprotonated by the solvent. The radicals then couple to form substitution products as well as react with solvent. The low yields of substitution product may be indicative of slow deprotonation of the toluene cation-radical by methanol.



Roth, Schilling and coworkers [47–54] have investigated the nuclear spin polarization behavior of cation-radicals of numerous strained hydrocarbon systems produced by PET to strong electron acceptors such as chloranil, anthraquinone and cyanoaromatics. These systems include cyclopentadiene dimers, methylenebicyclo[2.2.0]hexenes [48], bicyclo[1.1.0]butanes [49], hexamethyl (Dewar benzene) [50], norbornadiene [53], quadricyclene [53], and 1,2-diphenylcyclopropanes [54].

Formation of the high energy cation-radical species by PET produces C—C bond cleavage and rearrangements to form more stable cation-radical structures.

For example, hexamethyl (Dewar benzene) is converted to hexamethylbenzene by a radical-ion chain reaction initiated by PET to the sensitizer [50]. A similar PET induced rearrangement occurs in the transformation of a chloromethylenebicyclo[2.2.0]hexene to pentamethylbenzyl chloride [49].

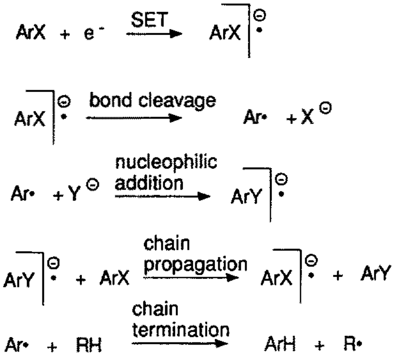


3 Reductive PET Bond Cleavages

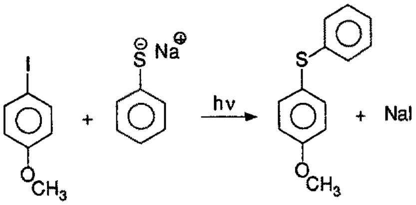
The first half of this chapter covered PET bond cleavage reactions resulting as a consequence of one-electron oxidation. In the following sections PET bond cleavage reactions resulting from one-electron reduction will be discussed.

3.1 Aryl Halides

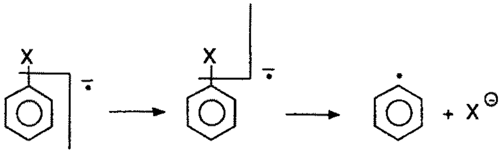
The best known PET bond cleavage reaction involves the substitution of aryl halides by the $S_{RN}1$ mechanism. This mechanism was first recognized by Bunnett and Rossi in 1970 [55]. The $S_{RN}1$ mechanism [56, 57] requires one-electron reduction of an aryl halide to initiate the substitution reaction. The anion-radical undergoes heterolytic carbon halogen (C–X) bond cleavage to form an aryl radical which reacts with a nucleophile such as phenylthiolate to produce a new anion-radical. This anion-radical then transfers an electron to another arylhalide in a chain propagating step forming the substitution product by a radical chain process. The initial electron source may be an electrode [58] or a photoexcited electron donor such as the nucleophile [59].



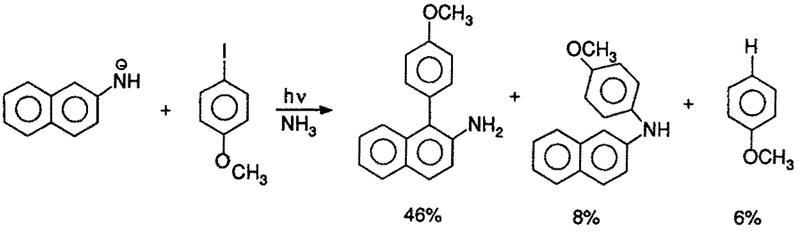
In a photostimulated reaction of phenylthiolate with *p*-iodoanisole *p*-methoxyphenyl phenylsulfide is produced in 76% yield [60]. Typical leaving groups may be Cl^-, Br^-, and I^- with the leaving group ability decreasing in the order I > Br > Cl > F [57]. Typical nucleophiles may be diphenylphosphide, $R\check{C}H-Z$, where Z is CN, COR, CO_2R or $CONR_2$ where R is an alkyl group or hydrogen as well as dialkyl arylphosphonate derivatives [57]. Phenyl X^-, where X is S, Se, Te are among the best nucleophiles in $S_{RN}1$ reactions due to their nucleophilicity and ablity to act as a source of electrons for the initiation step. Liquid ammonia, acetonitrile, dimethylsulfoxide and dimethylformamide are typical solvents for $S_{RN}1$ reactions. In general, an electron is added to the π^* molecular orbitals of an aryl halide to form an anion-radical. The lifetime of the anion-radical depends on the



leaving group and difference in energy between the π* and σ* molecular orbitals. It is speculated that the formation of the σ* anion-radical from the π* anion-radical may be required before fragmentation can occur.

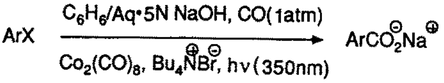


Recently, 2-naphthylamide anion was found to react with a number of aryl halides to provide mainly *C*-arylation in contrast to *N*-arylation [61]. Phenolate



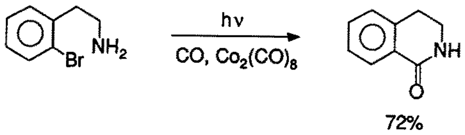
and naphtholate anions react similarly with aryl halides and form predominantly [62] biaryls.

Brunet, Sidot and Caubere [63] have demonstrated $Co_2(CO)_8$ catalyzed carbonylation of aryl and vinyl halides under phase-transfer catalysis (PTC) conditions only when the reaction medium is irradiated. A $S_{RN}1$ mechanism may be operative



$$\mathrm{ArX} \xrightarrow[\mathrm{Co_2(CO)_8,\ Bu_4\overset{\oplus}{N}\overset{\ominus}{Br},\ h\nu(350nm)}]{\mathrm{C_6H_6/Aq{\cdot}5N\ NaOH,\ CO(1atm)}} \mathrm{ArCO_2^{\ominus}Na^{\oplus}}$$

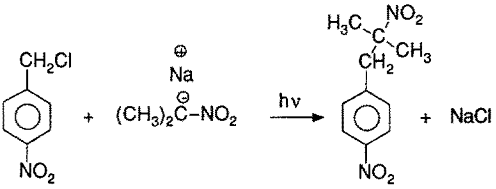
here. Benzolactams and benzolactones have been synthesized [63] by this PTC process as well.



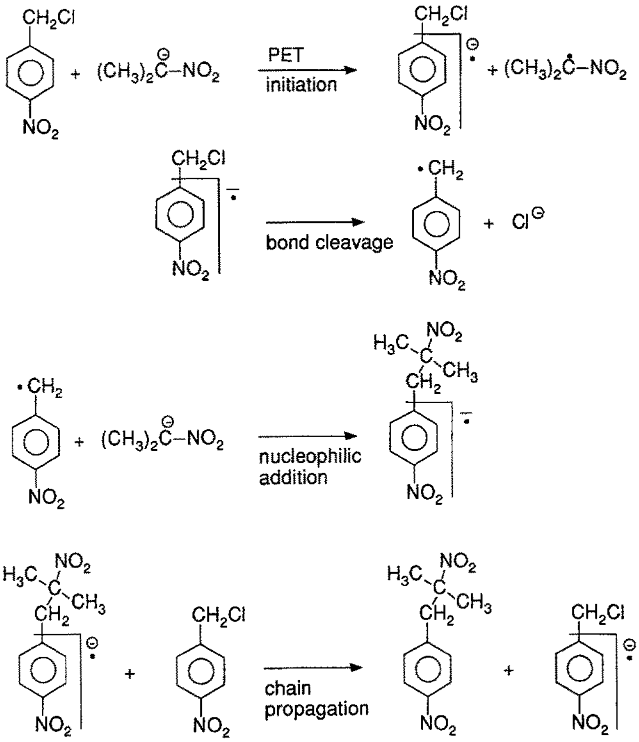
Selected $S_{RN}1$ reactions of alkyl and benzyl halides will be presented in the next section.

3.2 Alkyl and Benzyl Halides

Kornblum, in his investigations of the factors that control the course of ambident anion alkylation reactions [64, 65], found a new type of radical chain substitution reaction that involves anion-radicals and free radical intermediates. When *p*-nitrobenzylchloride, for example, was irradiated in the presence of the sodium salt of 2-nitropropane a 92% yield of *C*-alkylated product was observed unlike the alkylation of alkyl halides that gives predominantly *O*-alkylation. The first

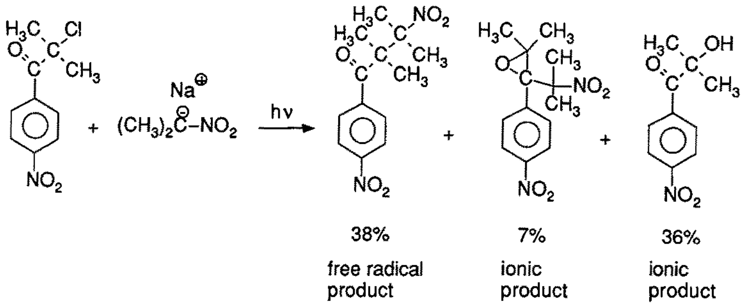


step in the reaction is PET or ET, if the reaction is initiated thermally, to form an anion-radical/radical pair. The *p*-nitrobenzylchloride anion-radical undergoes



a C—Cl bond cleavage reaction to form *p*-nitrobenzyl radical. This radical reacts with nitroalkyl anion to form a new anion radical species that can transfer an electron to the *p*-nitrobenzylchloride in a chain propagating step. The free-radical chain mechanism, which is now known as the $S_{RN}1$ mechanism is particularly evident in substitution reactions on the tertiary carbon in the *p*-nitrocumyl system [65].

Russell [65] has also been a major contributor to the field of photostimulated $S_{RN}1$ chemistry and has shown α-haloketones to react by this mechanism. 2-Nitropropyl anion reacts with 1,1-dimethyl-*p*-nitrophenacyl chloride to provide ionic and free radical chain product [66].



Russell [67] recently reported the PET C−X bond cleavage reactions of α-substituted nitroalkanes, e.g. $XC(CH_3)_2NO_2$ with X = Cl, Br, NO_2, $SO_2C_6H_5$, SAr and N_3, with alkoxide ions. The first step in the reaction is photostimulated ET from the alkoxide to the nitroalkane to produce a nitroalkane anion-radical which undergoes a C−X bond cleavage to produce a nitroalkane radical which reacts with alkoxide to provide a new anion-radical. The new alkoxynitro

$$XC(CH_3)_2NO_2 + RO^{\ominus} \xrightarrow[ROH]{hv} [XC(CH_3)_2NO_2]^{\ominus\bullet} + RO\bullet$$

$$[XC(CH_3)_2NO_2]^{\ominus\bullet} \xrightarrow[\text{bond cleavage}]{} (CH_3)_2\dot{C}NO_2 + X^{\ominus}$$

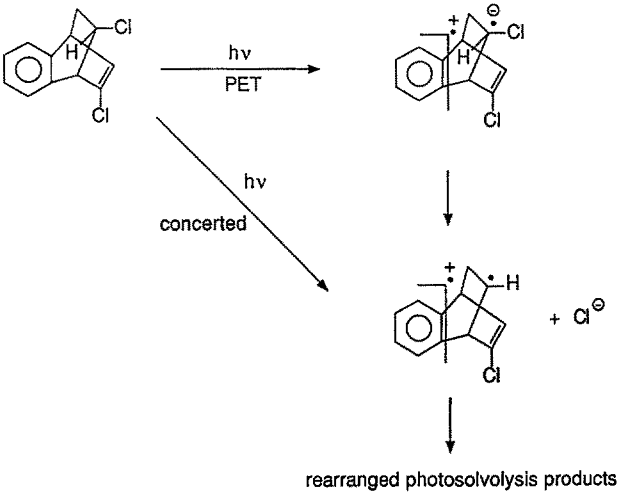
$$RO^{\ominus} + (CH_3)_2\dot{C}NO_2 \xrightarrow[\substack{\text{nucleophilic}\\ \text{addition}}]{} [ROC(CH_3)_2NO_2]^{\ominus\bullet}$$

$$XC(CH_3)_2NO_2 + [ROC(CH_3)_2NO_2]^{\ominus\bullet} \xrightarrow[\substack{\text{chain}\\ \text{propagation}}]{} ROC(CH_3)_2NO_2 + [XC(CH_3)_2NO_2]^{\ominus\bullet}$$

anion-radical can then transfer an electron to the starting material in a chain propagating step.

Cristol [68–75] and Morrison [76–82] have investigated the photochemically induced bond cleavage reactions of aryl chloroalkyl systems in which a photo-excited aryl ring induced ET to a σ* molecular orbital of a C−Cl bond initiates C−Cl bond cleavage chemistry and photosolvolysis. Saveant [83] has suggested that one-electron reductive cleavage of aliphatic halides occurs in a concerted process whereby bond breaking is concomitant with electron acceptance. The topic of concerted reductive cleavage reactions will be discussed further in Sect. 5.

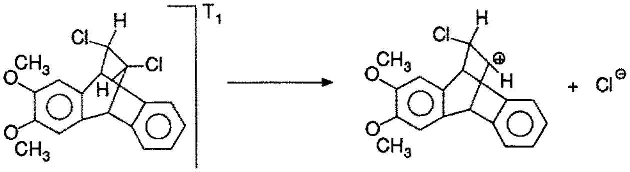
Photosolvolysis and photorearrangements have been observed by Cristol [69] in a chlorobenzobicyclo[2.2.2]octadienyl system. The orientation of the β-chloro group, which can be either *anti* or *syn* to the aryl ring is important in determining the propensity for PET bond cleavage. Photoexcitation of the aryl ring provides PET bond cleavage only in the molecule with an anti-chloro group.



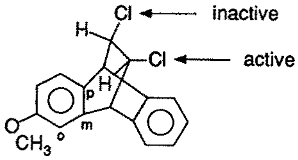
Photoexcitation of the benzene ring provides C – Cl bond cleavage in a concerted [83] or two-step process to produce a cationic species. Molecular rearrangement appears to follow two pathways to provide rearranged solvolysis products [69].

When the aryl ring is an efficient electron donor such as naphthalene or veratrole PET bond cleavage occurs in molecules containing both *syn*- and *anti*-C – Cl bonds [70] to produce photosolvolysis and rearrangement.

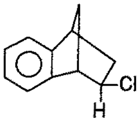
The transfer of excitation energy or an electron to the C – Cl bond is not well understood [71], however, the concept of PET from the aryl ring to the σ* of the C – Cl bond is reasonable based on the effect of substituents on the PET bond cleavage process. The *syn/anti* selectivity described previously is attributed to the proximity of the C – Cl σ* molecular orbitals to the π/π* molecular orbitals [71]. Photoexcited triplet states, formed through acetone sensitization, were found also to undergo PET bond cleavage, rearrangement and photosolvolysis provided the light absorbing chromophore is sufficiently electron rich, e.g. veratrole.



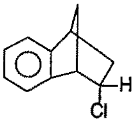
It was observed that an *anti*-homometa chloro group is selectively cleaved over that of an *anti*-homopara chloro group in the following bicyclic anisyl compound [74]. The "meta effect" in photochemistry was first demonstrated by Zimmerman and Sandel [84] and extended to the homometa situation by Cristol [81]. This effect was ascribed to the preponderance of electron density in anisole derivatives at the *meta* (and *ortho*) positions in the first excited state and its deficiency at the *para* position. In general, the compounds that undergo PET bond cleavage, rearrangement and photosolvolysis have shortened singlet lifetimes [75] and low fluorescence quantum yields, i.e., ~10^{-2}–10^{-4} times those of the corresponding compounds containing only hydrogens on the saturated bridges. These observations are consistent with PET from the π* molecular orbitals of the aromatic ring to the σ* molecular orbital of the C−X bond.



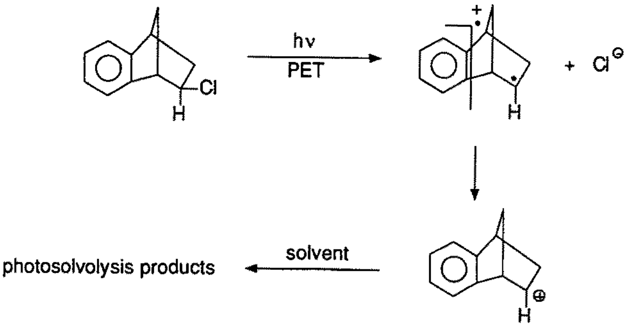
Morrison has been investigating the photolytic cleavage of remote functional groups in polyfunctional molecules [76–82]. A study of the photolysis of *exo*- and *endo*-2-benzonorborenyl chlorides shows the *exo*-chloride to exhibit a facile cleavage of the C−Cl bond upon excitation of the aryl chromophore with a rate >700 fold faster than that observed by the *endo* isomer [76]. The authors rationalize their observations by a correlation diagram which depicts the π, π* state as correlating with the diradical product state through an avoided crossing



exo



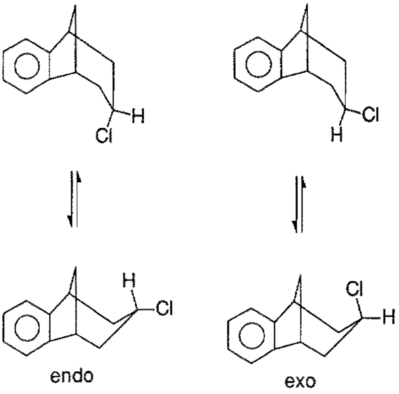
endo



with the C–Cl σ, σ* state [76]. Calculations indicate that avoided crossing is considerably larger and the barrier to reaction small when the C–Cl bond is *exo* rather than *endo* [76]. PET induced bond cleavage would also explain the experimental observations.

Photoinduced C–Cl bond cleavage has also been observed when the C–Cl bond is at the bridgehead position of 1,4-dichloro-7,7-dimethoxybenzonorbornene even though orbital overlap between the π* and σ* states was poor. The quantum efficiency for PET bond cleavage in this case was ~10–50 less than other homobenzylic C–Cl bonds [79].

In the *endo*- and *exo*-benzobicyclo[3.2.1]octen-3-yl chlorides PET bond cleavage produced an inverted reactivity pattern with the C–Cl bond now in the γ-position. The *endo*-isomer was observed to undergo C–Cl photocleavage ~ 10X faster than the *exo*-isomer. The variation in reactivity pattern was attributed to the favorable arylchlorine relationship in the *endo*-isomer which compensates for the increased aryl-γ carbon separation [81].

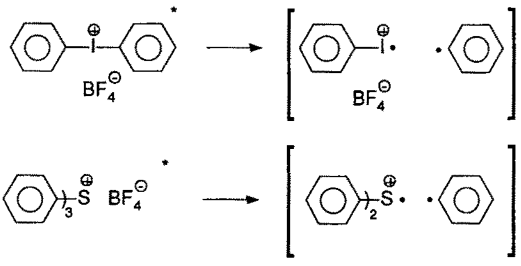


~10x rate increase

Morrison [78] has also investigated photolytic cleavage of C–Cl bonds in α- [82] and β-chloroketones [78]. These potential PET bond cleavage reactions are rationalized on the basis of a LUMO which is a combination of π* and σ* molecular orbitals. We have classified the intramolecular ET from a π HOMO to a π* or σ* LUMO as a PET process. A similar process occurs in the photolytic bond cleavage reactions of onium salts where the LUMO level is clearly σ* in character. This topic will be reviewed in the following section.

3.3 Onium Salts

Onium salts such as group 5 ammonium, phosphonium, arsonium, group 6 sulfonium, group 7 chloronium, bromonium and iodonium undergo PET bond cleavage reactions that is accompanied by the production of a Bronsted acid. The photochemically produced acid has been used effectively to initiate cationic polymerization [85] and other acid catalyzed chemistry. Photolysis of diaryliodonium and triarylsulfonium salts, for example, produces C—I and C—S bond cleavage to produce a cation-radical/radical pair [86]. The intermediates react with the solvent, medium or recombine [86] to produce acid by a bimolecular process. The LUMO level in these systems is σ* localized on the C—S (C—I) bond.

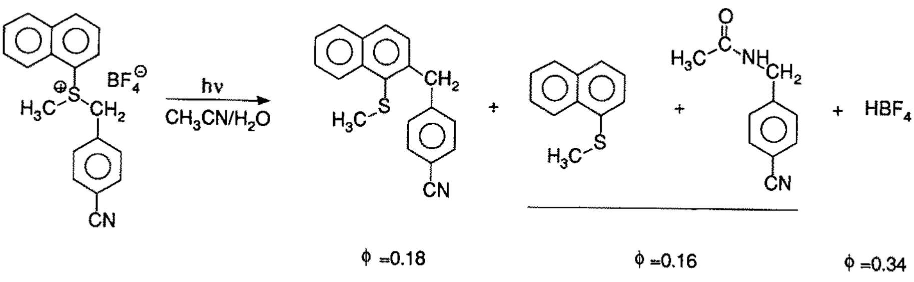


Photoexcitation of an electron from the π molecular orbitals on phenyl to the σ* molecular orbital produces C—S bond cleavage. the rate of bond cleavage is expected to be exceedingly fast and dependent on several factors including the thermodynamic stability of the cation-radical and radical species.

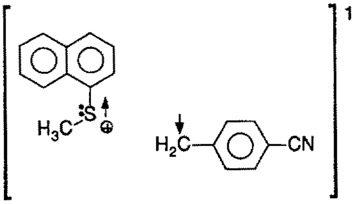
Intermolecular PET from photoexcited *N*-ethyl-2-ethylphenothiazine [87] and perylene [88], for example, to triphenylsulfonium salts produces C—S cleavage to provide diphenylsulfide and phenyl radical as well as the cation-radical of the sensitizer.

In this regard the electrochemical reduction behavior of arylmethylalkylsulfonium salts is of interest. One-electron reduction produces C—S bond cleavage by a concerted process. We believe that the sulfuranyl radical may be an intermediate in the one-electron reduction of sulfonium salts only when the cation-radical and radical species are extremely unstable. It has been concluded that as the electron enters the C—S σ* orbital bond cleavage occurs concomitantly [89].

The σ* nature of the LUMO level in sulfonium salts is, we believe, the fundamental scientific reason for their unique photochemical behavior. For example, photolysis of 1-naphthylmethyl-substituted alkyl sulfonium salts produce molecular rearrangement and photosolvolysis [90] as shown. The HOMO level is π in character localized on naphthalene and the LUMO is σ* localized on the

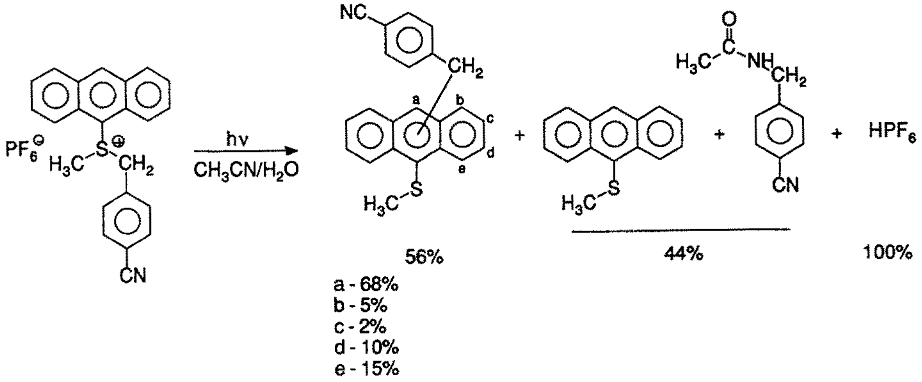


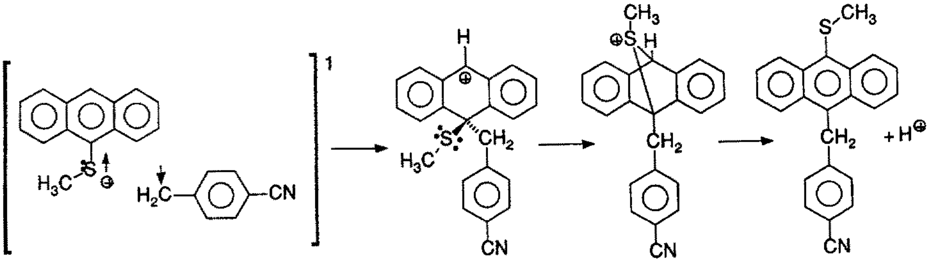
$S-CH_2$ bond as previously indicated. Photoexcitation produces $C-S$ bond cleavage to give a singlet in-cage cation-radical/radical pair. This intermediate can either produce in-cage radical coupling, i.e., rearrangement, or in-cage electron



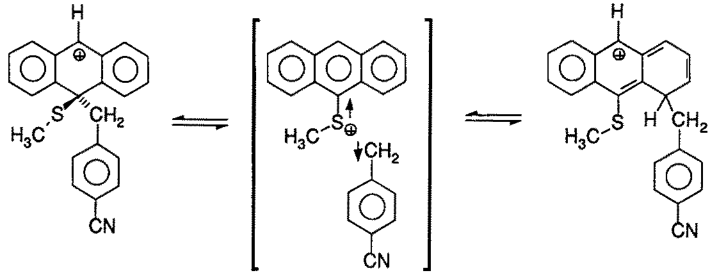
transfer if the thermodynamics for ET from the radical to the cation-radical is favorable to provide amide and 1-naphthylmethylsulfide.

By a similar mechanism the photolysis of 9-anthrylmethyl-*p*-cyanobenzylsulfonium hexafluorophosphate provided five regioisomeric rearrangement products along with photosolvolysis [91]. The preponderance of molecular rearrangement to position *a* was rationalized by the involvement of two competing rate processes [92]. the first process involves radical coupling at an aromatic carbon site containing a proton. We would expect the product distribution for this process to be similar to the spin density in the 9-thiomethylanthracene cation-radical. The





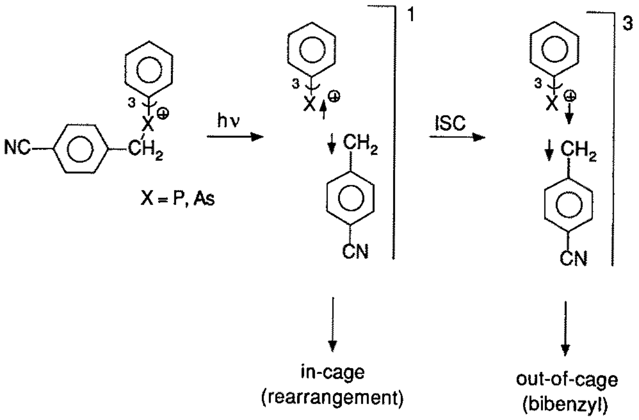
second process is one in which coupling occurs at the *ipso* carbon to provide an anthracene cation that can be stabilized by sulfur bridging. Transannular migration of the thiomethyl group with proton loss then produces the 9,10-disubstituted anthracene. The question of reversibility of an initially formed cation-radical/radical coupling product has not been resolved.



AM1 semiempirical molecular orbital calculations have been useful at predicting the nature of the LUMO level, i.e., σ^* or π^*, and PET bond cleavage propensity [92]. In a series of arylmethyl-*p*-cyanobenzylsulfonium salts where aryl is phenyl, 1-naphthyl, 9-anthryl and 5-naphthacenyl the LUMO level was calculated to be σ^* in each case except for the 5-naphthacenyl derivative. The lack of photochemistry in the 5-naphthacenyl derivative as well as fluorescent quantum yields, singlet lifetimes, and reduction potential behavior are consistent with the conclusions from the calculations [92].

Ammonium, phosphonium and arsonium salts may also possess a σ^* LUMO and undergo PET bond cleavage reactions to provide products that depend largely upon the heteroatom nuclear hyperfine coupling constant [93].

Ammonium and phosphonium salts with relatively large nuclear hyperfine coupling constants for N and P provide only out-of-cage products, i.e., bibenzyl. While an arsonium salt, on the other hand, provides mainly in-cage radical coupling, i.e., rearrangement, due to a smaller nuclear hyperfine coupling constant

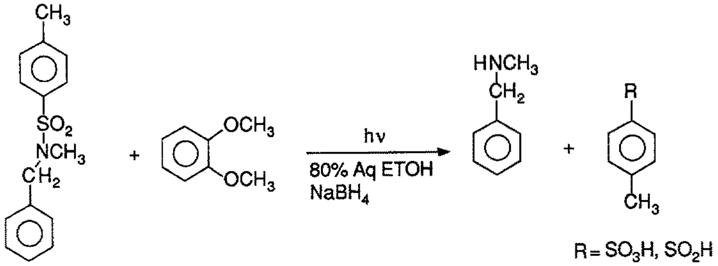


for As. The heteroatom nuclear spin enhances the rate of intersystem crossing (ISC) of the singlet cation-radical/radical pair to the triplet pair to provide out-of-cage photoproducts.

The next section will be concerned with the selective removal of arylsulfonyl groups in *N*-tosylamines by a PET process.

3.4 Tosylamines

Yonemitsu and coworkers [94] have described the removal of *p*-toluene and naphthalene sulfonyl protecting groups in arylsulfonylamines by a PET bond cleavage process. For example, *N*-tosylamines were irradiated in aqueous ethanol in the presence of an electron-donating aromatic molecule and a reductant such as sodium borohydride, ascorbic acid or hydrazine to provide the deblocked amine.

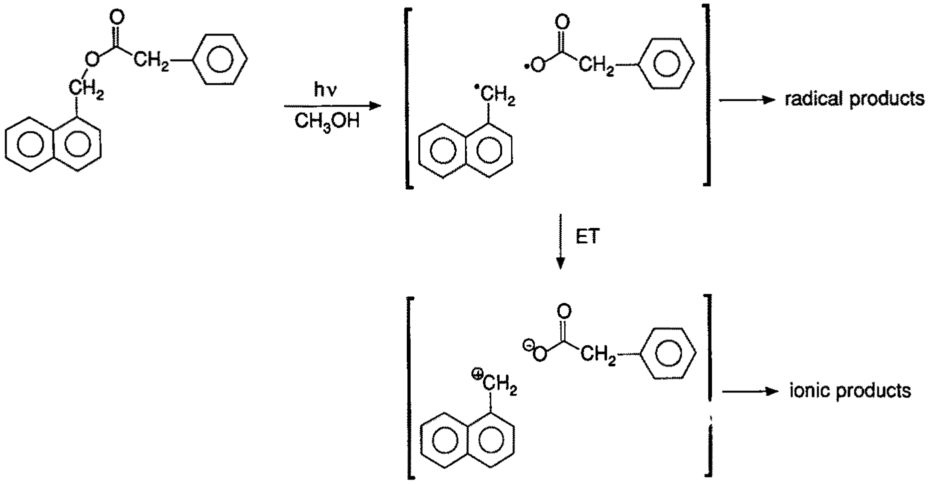


The authors suggest that the photoexcited electron donor transfers an electron to the sulfonyl group of the tosylamine to provide an anion-radical that undergoes a heterolytic S – N bond cleavage to produce the deblocked amine after protonation as well as tosylsulfonic and sulfinic acid. The function of the reducing agent is to reduce species such as the dimethoxybenzene cation-radical and the sulfonyl radical.

Aryl esters have recently been observed to undergo photoinduced bond cleavage reactions to provide a product ratio that depends upon the redox behavior of the initially formed intermediates.

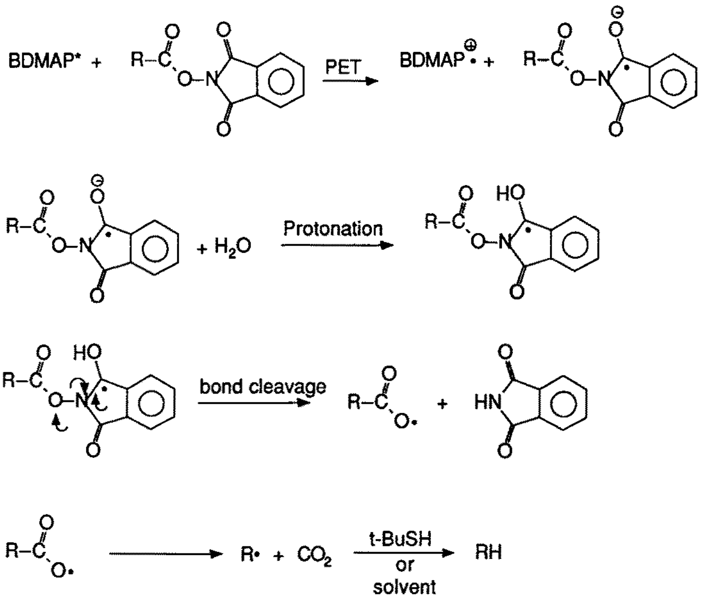
3.5 Esters

Pincock and DeCosta [96] have recently described photoinduced bond cleavage reactions in a series of naphthylmethyl esters to produce both ionic and radical products. The authors attribute their results to excited state homolysis to form a caged radical pair and ET between the radicals to form an ion pair. The rates of ET have been rationalized by the Marcus theory which shows a Marcus inverted region where ET becomes slow when ΔG^0_{ET} is highly exothermic. In this case ET appears to follow homolytic bond cleavage rather than prior to bond breaking.



3.6 *N*-Acyloxyphthalimides

Okada, Okamoto and Oda [97] have recently described a novel method of decarboxylation through a PET bond cleavage process in *N*-acyloxyphthalimides. A photoexcited electron donor such as 1,6-bis(dimethylamino)pyrene (BDMAP) transfers an electron to the phthalimide to produce an anion-radical that is protonated to form a radical prior to homolytic N—O bond cleavage. Bond



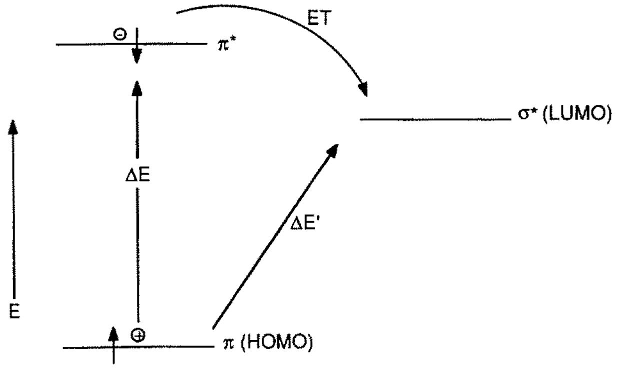
cleavage produces phthalimide and a carboxyl radical. The carboxy radical decarboxylates to form an alkyl radical that abstracts a hydrogen atom from a hydrogen atom source such as *t*-BuSH. This process could also be used to initiate free radical polymerization.

4 Bond Cleavage from $\pi \rightarrow \sigma^*$ Photoexcitation

In a molecular system which clearly possess a σ^* LUMO the photoexcitation process may involve promotion of an electron from a π HOMO to the σ^* LUMO. This process may or may not produce bond cleavage. Direct observation of a $\pi \rightarrow \sigma^*$ electronic transition is often difficult due to the localized nature of the σ^* molecular orbitals resulting in a low probability for the transition [91]. More likely a $\pi \rightarrow \pi^*$ electronic transition takes place initially and ET, i.e., $\pi^* \rightarrow \sigma^*$, is required to eventually populate the lower energy σ^* antibonding molecular orbital. Onium salts are examples of chemical structures that possess a σ^* LUMO and are expected to behave in this manner (see in Sect. 3.3).

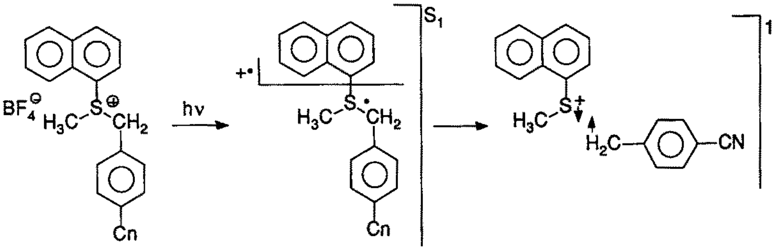
We would like to present a more detailed discussion of bond cleavage reactions in systems that clearly have a σ^* LUMO as well as those molecular species that have a LUMO that is a combination of π^* and σ^*.

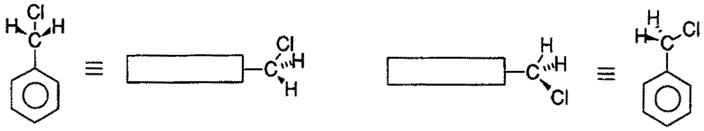
Certain arylalkylbenzylsulfonium salts appear to possess a σ^* LUMO and undergo photolytic bond cleavage provided the energy of the absorbed photon is greater than the energy of the bond being broken.



Homolytic bond cleavage as a result of $\pi \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ photoexcitation produces a singlet cation-radical/radical pair that can recombine to produce starting material, molecular rearrangement, undergo intersystem crossing to the triplet pair or ET to form the benzyl carbocation. A possible description of the π/σ^* excited state is represented below. The rate of bond cleavage must be competitive with back ET.

In comparison, benzyl halides, for example, possess a LUMO that is delocalized over both the π^* and σ^* molecular orbitals and the degree of overlap is strongly dependent on the orientation of the C—Cl bond relative to the π framework of the benzene ring. A dihedral angle of 90° between the C—Cl bond and aromatic ring provides maximum overlap between the π* and σ* molecular orbitals while 0° dihedral angle provides minimum overlap. It is expected that bond cleavage will take place from the conformational isomer with the maximum π*/σ* overlap and ability to stabilize the benzyl radical product by efficient *p*-orbital overlap.





90° dihedral angle
max π*σ* overlap

0° dihedral angle
min π*σ* overlap

5 Concerted PET Bond Cleavage

Intuitively, one would expect concerted PET bond cleavage reactions to be more efficient than nonconcerted or two-step bond cleavage processes due to the elimination of back ET in the former case. This general conclusion may or may not be true.

It is believed that the electrochemical reductive of aliphatic halides [58], benzyl halides and aryldialkylsulfonium salts [89] are concerted, i.e., electron acceptance is concomitant with bond cleavage, due in part to the σ* nature of the LUMO as well as the instability of the anion-radical species and stability of the products. If the anion-radical is not a discrete chemical entity back ET cannot take place. Therefore, the efficiency of PET bond cleavage reactions would be expected to be greater for the reasons mentioned above. However, due to the localized nature of the σ* molecular orbitals the probability for intermolecular and intramolecular ET, for example, to a σ* MO may be quite low. However, the overall efficiency of PET concerted bond cleavage reactions may approach unity provided that ET to the σ* LUMO does indeed occur. This topic clearly requires further consideration and research using fast kinetic laser spectrophotometric techniques to go beyond the qualitative discussion provided here.

6 Acknowledgements

Discussions with Professor David Whitten concerning PET bond cleavage reactions are gratefully acknowledged.

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Photoinduced Electron Transfer of Carbanions and Carbocations

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Table of Contents

This chapter reviews electron transfer reactions that arise from direct photochemical excitation of carbanions and carbocations or from carbanions and carbocations generated via an initial photochemical reaction. The types of carbanions and carbocations treated will be primarily (but not restricted to) those with hydrocarbon frameworks. Electron transfer

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Topics in Current Chemistry, Vol. 156

from photoexcited iminium and onium ions and related compounds (which are formal carbocations) are not included since these reactions are discussed in chapters 1.7 and 1.8 of this monograph, respectively. This chapter has two principal sections for the two types of intermediates under review. Each section will begin with a consideration of the excited states available and reasons as to why the excited states of these species might be expected to undergo electron transfer reactions. This will be followed by a discussion of examples from the literature classified under their structural type.

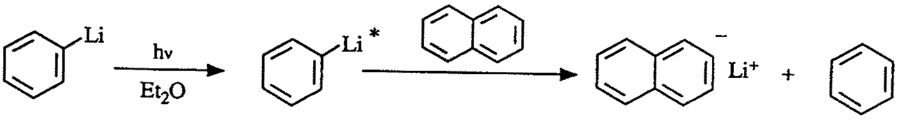
1 Photoinduced Electron Transfer Reactions of Carbanions

The photochemistry of carbanions in general has been reviewed by Tolbert [1–3] and Fox [4]. These reviews may be consulted for much of the earlier studies of electron transfer reactions of photoexcited carbanions, as well as other types of photochemical reactions of these species. In addition, they [1–4] summarize the spectroscopic characteristics of the commonly accessible carbanions. Carbanions in general absorb at longer wavelengths than the corresponding neutral carbon acid. The red shifts observed can be as large as several hundred nm. Because of their long wavelength absorption, direct photolysis is an easy matter but triplet sensitization studies cannot usually be carried out. Thus it is generally difficult to sort out the multiplicity of the reactive state in carbanion photochemistry.

In much the same way that photoexcited neutral aromatic compounds are better electron acceptors and donors than the corresponding ground state, photoexcited carbanions would be expected to be good electron donors. The added electron-electron repulsion inherent in carbanions facilitates this even more so. Thus electron transfer (photoejection or photodetachment) from photoexcited carbanions is a common primary reaction pathway. The resulting chemistry is that of the radical. Photodetachment of carbanions in the gas phase has been studied by Brauman and coworkers [5] who have shown that photodetachment can occur by irradiating at wavelengths longer than the excitation energy of the carbanion. In general, carbanions in solution are less prone to photodetachment compared to the situation in the gas phase [1–4]. Increased conjugation of the carbanion, e.g., by aromatic rings, also decreases photodetachment efficiency [1–4].

1.1 Aryl Carbanions

The study of the photochemistry of aryl carbanions has been restricted to aryllithiums with only a limited number of studies available. Hence, a general picture of their photochemistry is not available at this time. Photolysis of phenyllithium in the presence of aromatic hydrocarbons such as naphthalene, biphenyl, phenylene, etc. in diethyl ether results in electron transfer from the phenyllithium to the aromatic hydrocarbon, with production of the corresponding hydrocarbon radical anion, as observed by ESR spectroscopy [6–8] (Eq. 1). Photolysis of phenyllithium or 2-naphthyllithium alone gave the corresponding biaryl products and metallic lithium [9–10]. For this reaction, it is possible to write a mechanism which does not require electron transfer from the anion [9, 10],

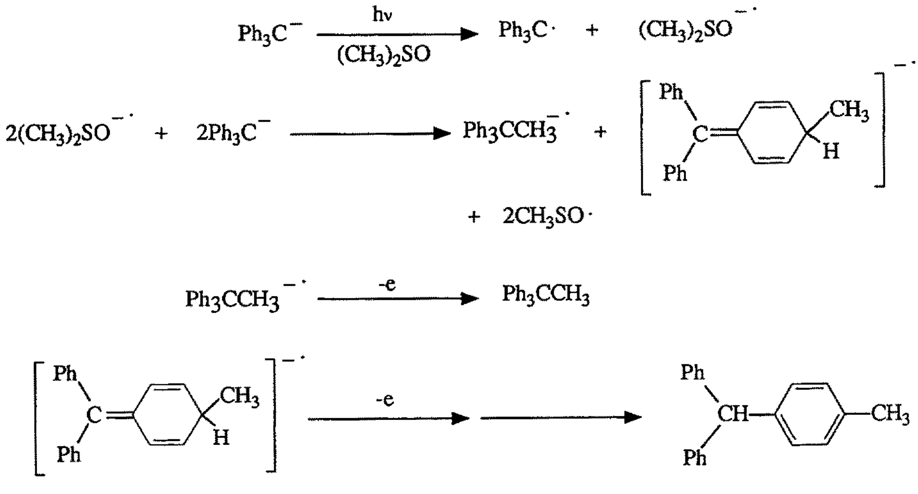


(1)

viz. by initial generation of a phenyl radical via C—Li bond homolysis, followed by phenyl radical attack on unreacted aryllithium, which on loss of Li atom gives the biaryl product. Thus electron transfer from photoexcited aryllithiums does not appear to be a general process, but depends very much on the reaction conditions.

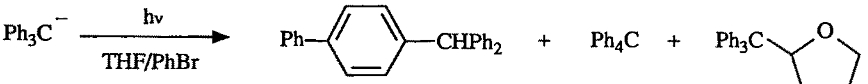
1.2 Arylmethyl Carbanions

Because arylmethyl carbanions are generally more accessible and their photo-induced electron transfer reactions more readily characterized, these anions have been studied to a much larger extent than aryl carbanions. In this section, only direct photolysis of simple arylmethyl anions will be reviewed. Those arylmethyl anions which have additional stabilizing structural features such as the presence of an allylic or a fluorenyl system are discussed later under a separate section. Tolbert [1–3] has shown that successive replacement of the hydrogens of methyl carbanion by a phenyl substituent (i.e., $CH_3^- \rightarrow PhCH_2^- \rightarrow Ph_2CH^- \rightarrow Ph_3C^-$) not only shifts the absorption maximum to longer wavelength (i.e., decrease in excitation energy) but also increases the electron affinity of the corresponding radical. In other words, as the carbanion is successively more stabilized by phenyl substituents, the tendency for electron photodetachment decreases, in the absence of other factors. Nevertheless, photolysis of triphenylmethyl anion in dimethyl sulfoxide (DMSO) results in products which arises via initial electron transfer from the carbanion to DMSO [11–15] (Scheme 1). The same anion is photochemically inert in the absence of DMSO or other electron acceptors [14]. Photolysis of triphenylmethyl anion in the presence of an aryl halide as electron acceptor results in a radical chain $S_{RN}1$ reations [15, 16]. For example, photolysis of the anion in the presence of bromobenzene gave the product distribution shown



Scheme 1

in Eq. 2, with the para-phenylated compound 1 being tne major product [2, 15, 16]. The primary event in this reaction is the photoinduced electron transfer from the carbanion to the aryl halide, to generate triphenylmethyl radical and the radical anion of the aryl halide. Loss of halide ion from the aryl halide radical anion gives a phenyl radical, which reacts with the carbanion to give a new radical anion, which can propagate the chain process [2, 15, 16]. The (4-biphenyl)diphenylmethyl anion can undergo similar photochemistry, but with greatly reduced efficiency [2, 11, 12]. Use of *t*-butylmercury chloride as electron acceptor in the photolysis of the triphenylmethyl anion results in chemistry similar to that observed in Scheme 1 [17], with the *t*-butyl radical replacing the methyl group in the products observed.



1 (major)

(2)

With regards to the dynamics of the electron photodetachment process in solution, Szwarc and coworkers [18–21] have carried out a number of studies using flash photolysis on the 1,1,4,4-tetraphenyl-1,4-butane dianion 2 (and other anions), which on photolysis gives the monoanion via electron ejection, followed by a series of steps which eventually gives back the initial dianion (Scheme *2*). Rates of electron transfer to $Ph_2C=CH_2$ as well as dimerization of $[Ph_2C-CH_2]^{-\cdot}$(to give *2*) have been measured with different counterions. In general, however, it is fair to say that the details of the electron ejection process from photoexcited carbanions remain largely unexplored. For example, does electron ejection occur from a discrete excited state or does it occur "spontaneously" with excitation? The exact mechanism may depend on various parameters such as structure of the carbanion and the solvent used. However, with the advent of powerful picosecond flash techniques, such questions can now be addressed.

$$\underset{\mathit{2}}{Na^+\,Ph_2\overset{-}{C}\text{-}CH_2CH_2\text{-}\overset{-}{C}Ph_2\,Na^+} \xrightarrow{h\nu} Na^+\,Ph_2\overset{-}{C}\text{-}CH_2CH_2\text{-}\overset{\cdot}{C}Ph_2 + Na^+ + e^-$$

$$Na^+\,Ph_2\overset{-}{C}\text{-}CH_2CH_2\text{-}\overset{\cdot}{C}Ph_2 \longrightarrow Ph_2C{=}CH_2 + Ph_2\overset{-}{C}\text{-}\overset{\cdot}{C}H_2\,Na^+$$

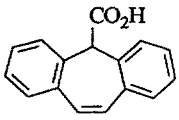
$$Ph_2C{=}CH_2 \xrightarrow[+e^-]{Na^+} Ph_2\overset{-}{C}\text{-}\overset{\cdot}{C}H_2\,Na^+$$

$$2\,Ph_2\overset{-}{C}\text{-}\overset{\cdot}{C}H_2\,Na^+ \longrightarrow \underset{\mathit{2}}{Na^+\,Ph_2\overset{-}{C}\text{-}CH_2CH_2\text{-}\overset{-}{C}Ph_2\,Na^+}$$

Scheme 2

1.3 Photogenerated Dibenzannelated Carbanions

In this section we will discuss those photochemical reactions which give rise to the titled carbanions, which can subsequently undergo electron transfer reaction from an excited state. Examples of this type of photoinduced electron transfer reaction are not common because it requires either (i) that the carbanion is photogenerated adiabatically and hence can undergo electron ejection or (ii) that the carbanion photogenerated is sufficiently stable to be long-lived enough to absorb a second photon and hence result in electron ejection. Wan and coworkers [22, 23] have reported two methods for the photogeneration of dibenzannelated carbanions: photodecarboxylation [22] and photochemical C—H bond heterolysis [23] (excited state carbon acids). Photolysis [22] of dibenzannelated acetic acids *3–8* in aqueous solution (pH > pK_a) results in decarboxylation to give the corresponding protonated products with quantum yields in the range 0.06 to 1.0. Photolysis in D_2O solution gave the corresponding α-deuterated products, which is indicative of a mechanism via initial formation of a carbanion intermediate.



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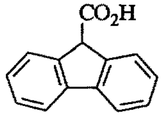

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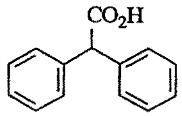

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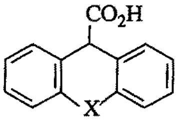
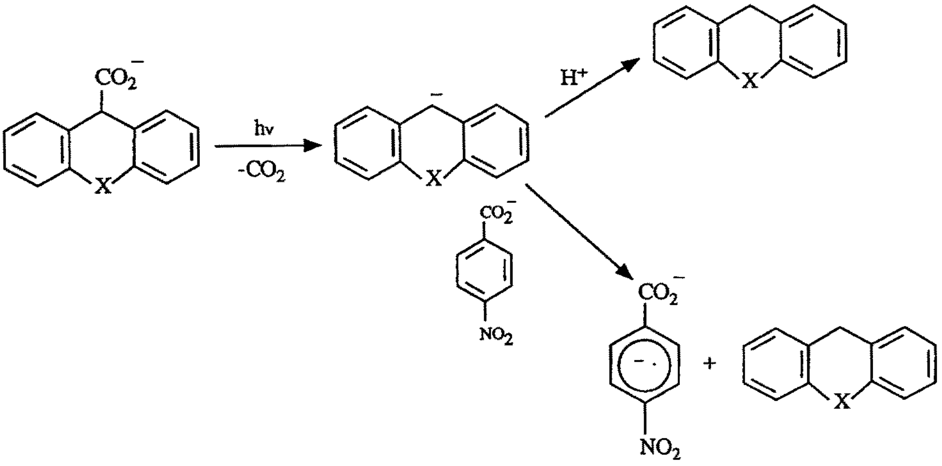


6 X = CH_2CH_2
7 X = O
8 X = S



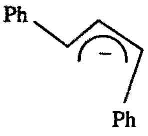
Scheme 3

Photolysis in the presence of a good electron acceptor such as *p*-nitrobenzoate (PNB) results in formation of the PNB radical dianion, as detected by ESR spectroscopy, which is indicative of an electron transfer reaction. No ESR signals were observed in the dark or on photolysis of PNB solution alone. The efficiency of PNB radical anion generation correlated with the efficiency of photodecarboxylation, i.e., the greater the quantum yield of photodecarboxylation, the stronger the ESR signal of PNB radical anion observed. Scheme 3 has been proposed [22] to account for these observations. The electron transfer step is believed to take place from the photogenerated carbanion to PNB. It is unknown whether the carbanion is formed adiabatically. The lack of radical derived products (e.g., dimers from the radical in Scheme 3) suggests that electron transfer is a minor reaction pathway for photogenerated benzannelated carbanions: they are protonated rapidly by the solvent, and therefore are believed to be very short lived. The same sort of electron transfer may also be possible for benzannelated carbanions photogenerated via C–H bond heterolysis [23] although only one system so far, that of suberene, has been shown to undergo observable C–H bond ionization.

1.4 Arylallyl Anions

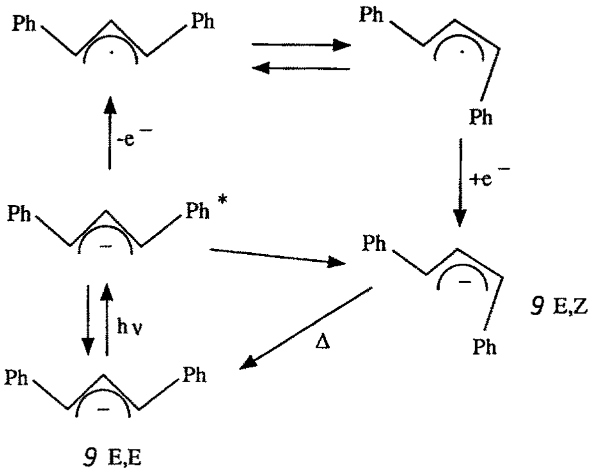
Tolbert [1–3] has summarized the various photochemical pathways open to allyl anions in general, including electron photoejection. Other pathways include ring closure to a cyclopropyl anion, *E*-*Z* isomerization, protonation and α-bond cleavage. With the availablity of a greater number of photochemical pathways for allyl anions in general, it is not surprising that electron photoejection is not an important pathway for aryl-stabilized allyl anions. One of the most studied arylallyl anions is 1,3-diphenylallyl anion *9*. This anion undergoes thermal isomerization between the more stable *E*,*E*-isomer and the less stable *E*,*Z*-isomer. At low temperature, the thermal isomerization is sufficiently slow to allow the photochemical isomerization to be studied [24–26]. Thus photolysis of the more stable *E*,*E*-isomer gives rise to the *E*,*Z*-isomer, which reverts back to the *E*,*E*-isomer on warming. With regards to the mechanism of the photoisomerization, one could envisage a simple pathway involving deactivation of the photoexcited *9* *E*,*E*-isomer by bond rotation, to give *9* *E*,*Z*, similar to the mechanism of photoisomerization of neutral alkenes. However, a second mechanism which must be considered in light of what is known about carbanion excited states involves

9 E,E

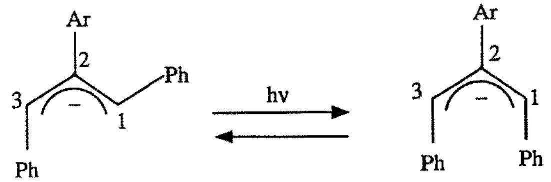


9 E,Z

initial electron ejection from the carbanion, to give the 1,3-diphenylallyl radical, which can undergo twisting to the isomeric radical, which on electron capture, gives the *E,Z* isomer of the anion (Scheme 4). The low activation barrier for bond rotation in the 1,3-diphenylallyl radical makes the electron ejection mechanism attractive [27]. Efforts have been directed to distinguish between these two mechanisms [1, 3, 28, 29]. Tolbert and Ali [28] have studied the photoisomerization of 2-aryl-substituted-1,3-diphenyl anions 10 (Eq. 3) with the aim of testing the effect of substituents at the 2-position on isomerization efficiency. They reasoned that since the non-bonding MO of allyl anion or radical has a zero coefficient at C-2, the presence of a C-2 substituent should not perturb the energy of this MO in the Hückel approximation. Thus if the mechanism of photoisomerization involves initial electron ejection (with the electron coming from this non-bonding MO), then the efficiency of photoisomerization should not be much affected by the C-2 group, keeping other features such as steric effects the same. However, should the photoisomerization proceed via a bound excited state, substituents at C-2 should have a strong effect on the efficiency since the anti-bonding MO has a large coefficient at C-2. The observations [1, 3, 28] are consistent with a mechanism involving a bound excited state since the photoisomerization efficiency had a



Scheme 4



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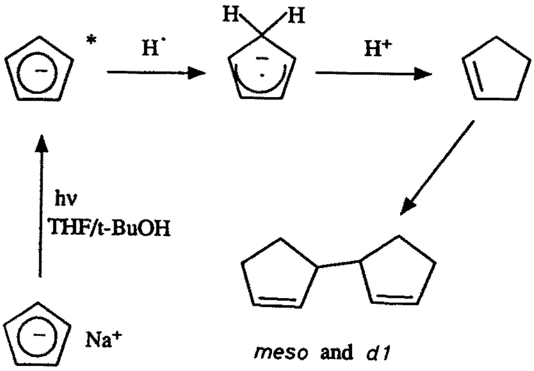
strong dependence on the C-2 group. In support of this conclusion, Brocklehurst and coworkers [29] in a recent study have measured Arrhenius parameters for photoisomerization of 9 *E,E* and related compounds and have concluded that the results are incompatible with a mechanism of photoisomerization involving initial electron loss. Many other types of arylallyl anions also appear to avoid electron ejection as a primary pathway. For example, the phenallenyl anion photocyclizes to give cyclopropa-acenaphthene [30] and 1,1,3,3-tetraphenylpropenyl anion undergoes photopromoted H/D exchange at C-2 [1] in the presence of *t*-BuOD. However, when photolyzed in DMSO, electron transfer occurs, resulting in methylation, to give 1,1,3,3-tetraphenyl-1-butene as the product [11].

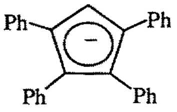
1.5 Cyclopentadienyl and Related Carbanions

Photolysis of sodium cyclopentadienide in 20% *t*-butyl alcohol-80% tetrahydrofuran gave meso and dl-3-(3′-cyclopentenyl)cyclopentenes [31] (Scheme 5). The postulated mechanism (Scheme 5) involves hydrogen abstraction from the photoexcited cyclopentadienide anion, to give the radical anion. Subsequent protonation gives the cyclopentenyl radical, which on dimerization gives the observed product. No electron transfer step is invoked. When perdeuteriocyclopentadienide was photolyzed in 20% *t*-butyl alcohol-O-D/80% tetrahydrofuran, the 3,3′-dicyclopentenyls observed were perdeuterated. This observation raises doubts about the suggested mechanism of reaction presented in Scheme 5 since one would have to invoke hydrogen atom abstraction from the hydroxyl proton of *t*-butyl alcohol rather than from the more favored methyl groups or from the methylenes of tetrahydrofuran cosolvent. Unfortunately, no additional studies have been reported on this curious reaction.



Scheme 5

Electron transfer has been invoked in the photochemistry of tetraphenylcyclopentadienide anion *11* in DMSO, which gave the dimethylated product *12*, in addition to dimeric coupling products [32]. The mechanism of reaction is similar to that shown in Scheme 1 for photolysis of triphenylmethyl anion in DMSO, in which the first step is electron transfer from the anion to DMSO. Photolysis of *11* in tetrahydrofuran alone gave no photochemistry. However, on the addition of TiO_2 (a semiconductor acting as the electron acceptor), the dimer *13* was observed on photolysis. Similar photochemistry was observed for the fluorenyl anion *14* [32]. Thus photolysis of *14* in tetrahydrofuran alone gave no photochemistry. On the addition of TiO_2, photolysis gave bifluorene *15*. Photolysis of *14* in DMSO gave 9,9-dimethylfluorene *16* [32]. In a similar study, Tolbert [11] has shown that photolysis of 9-methylfluorenyl and 9-phenylfluorenyl anions in DMSO results in methylation at the 9-position. These studies suggest that carbanions of this type undergo electron photoejection only in the presence of an electron acceptor. However, Huber [33] has shown that photolysis of *14* in 2-methyltetrahydrofuran gave the radical anion of fluorene, as observed by ESR spectroscopy. It was claimed [33] that the initial reaction step involves electron photoejection from the fluorenyl anion *14* to fluorene. However, there was no mention of observing bifluorene *15*, as required if this mechanism was operative.



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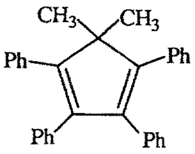

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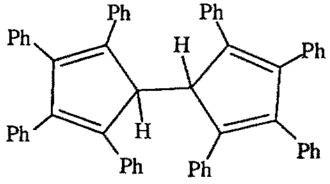

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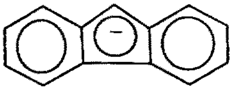

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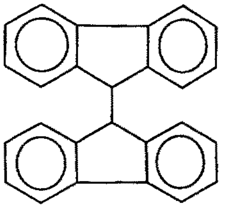

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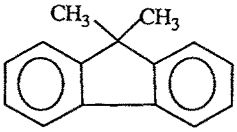
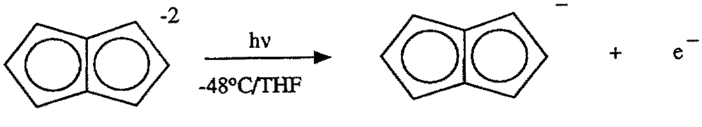


16

A system in which electron photoejection has been observed without inference from product studies is in the photolysis of the pentalene dianion *17* (Eq. 4), which gave the pentalene radical anion in tetrahydrofuran [34], as characterized by ESR spectroscopy. This radical anion was previously inaccessible. In the dark, the radical anion reverts back to the dianion by electron capture.



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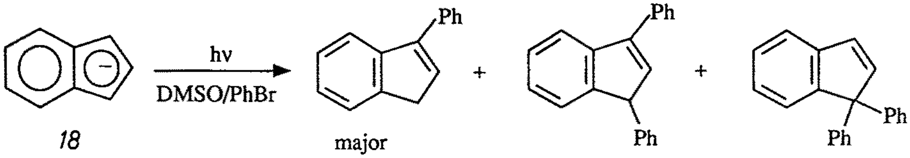
(4)

The photochemistry of the indenyl anion *18* and related compounds in DMSO solution with added bromobenzene as electron acceptor has been studied in detail by Tolbert and Siddiqui [35]. Photolysis of these systems in the presence of bromobenzene results in phenylation (Eq. 5), the mechanism of which involves



18

major

(5)

initial electron transfer from photoexcited *18* to bromobenzene (Scheme 6; In = indenyl), via a non-chain photostimulated $S_{RN}1$ [16] pathway. The regiochemistry of the phenylation has been studied in detail and is attributed to phenyl attack at the most basic site of the indenyl anion *18*. In the absence of electron acceptors, the indenyl anion *18* does not exhibit any permanent photochemistry.

$$\mathrm{In}^{-} \xrightarrow{h\nu} \mathrm{In}^{-*}$$

$$\mathrm{In}^{-*} + \mathrm{PhBr} \longrightarrow \mathrm{In}^{\bullet} + \mathrm{PhBr}^{-\bullet}$$

$$\mathrm{PhBr}^{-\bullet} \longrightarrow \mathrm{Ph}^{\bullet} + \mathrm{Br}^{-}$$

$$\mathrm{Ph}^{\bullet} + \mathrm{In}^{-} \longrightarrow \mathrm{InPh}^{-\bullet}$$

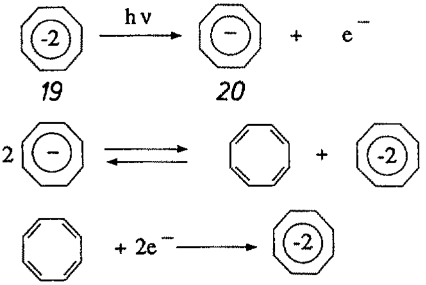
$$\mathrm{InPh}^{-\bullet} + \mathrm{In}^{\bullet} \longrightarrow \mathrm{InPh} + \mathrm{In}^{-}$$

$$\mathrm{In}^{\bullet} + \mathrm{In}^{\bullet} \longrightarrow \mathrm{In\text{-}In}$$

Scheme 6

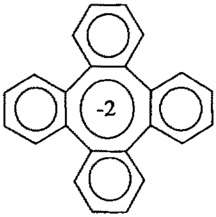
1.6 Cyclooctatetraenyl Dianion

The cyclooctatetraenyl dianion *19* (COT^{-2}) is an aromatic 10π electron system and hence can be readily prepared from cyclooctatetraene by reduction (alkali metals or electrochemically). An early report [36] of the photochemistry of COT^{-2} in the presence of weak acids such as amines and terminal alkynes showed that it is protonated in the excited state (to give the monoanion): COT^{-2} is more basic in the excited state than in the ground state. However, in the absence of such weak acids, photolysis of COT^{-2} results in electron photoejection [37–39]. The electron photoejection process and subsequent chemistry has been studied in solution [37], in a glass [38] and on semiconductor electrodes using COT^{-2} derivatives [38]. Scheme 7 depicts the reaction scheme for photolysis of *19* [40, 41]. Initial excitation of *19* results in electron ejection, to give the radical anion *20* (COT^{-}). Disproportionation of two molecules of *20* gives back *19* and cyclooctatetraene. Electron capture by cyclooctatetraene also gives back *19*. Thus the initial electron ejection results in the transient generation of electrons and *20*, but there is an inherent driving force for overall back electron transfer, to give *19*. Levin and Szwarc [37] have studied the kinetics of the disproportionation reaction of *20* with different cations in several solvents. The anion *20* was photogenerated by flash photolysis. They found that the rate constant for disproportionation was very dependent on cation and solvent, with a range of six orders of magnitude in reactivity. Dvorak and Michl [38] have used the electron photoejection of *19* to generate *20* in 2-methyltetrahydrofuran glass at 77 K. The dynamics of the photogenerated ion pair ($M^{+}COT^{-}$) were subsequently studied and its spectroscopic properties characterized. Hohman and Fox [39] have utilized COT^{-2} derivatives attached to semiconductor electrodes as part of a photoelectrochemical cell. Irradiation of the electrode resulted in the generation of a photocurrent. The mechanism of photocurrent production and possible use as a solar energy conversion device are discussed.



Scheme 7

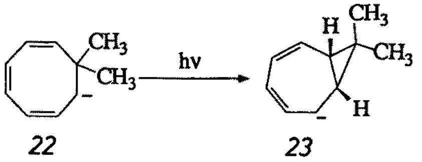
The electron photoejection of tetrabenzocyclooctatetraene dianion *21* (a derivative of *19*) in 2-methyltetrahydrofuran has been reported by Huber [33]. The photogenerated radical ion was characterized by ESR spectroscopy. In the dark, reverse electron transfer to give back *21* was observed.



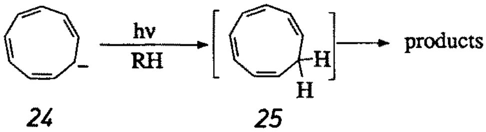
21

1.7 Other Cyclic Anions

Compared to the cyclooctatetraenyl dianion *19*, other cyclic anions (besides cyclopentadienyl anions discussed in Sect. 1.5) have received considerably less attention. Of those that have been studied, not all of them display electron photoejection as a reaction pathway. For example, the 8,8-dimethyl-2,4,6-cyclooctatrienyl anion *22* undergoes cyclization to give 8,8-dimethylbicyclo[5.1.0]octa-3,4-dienyl anion *23* on photolysis as the exclusive photochemical pathway [42] (Eq. 6). Photolysis of the cyclononatetraenyl anion *24* results in protonation of the more basic excited state anion, to give transient *cis*, *cis*, *cis*, *cis*-1,3,5,7-cyclononatetraene *25* (Eq. 7), which subsequently undergoes intramolecular cyclization to give several cyclized products [43]. Electron photoejection is not observed. However, the behavior is quite different for the cyclooctadienyl anion *26*. The photochemistry of this anion has been studied by Fox and Singletary [44], who report that it has great propensity for undergoing electron photoejection, unlike what is observed for anions *22* and *24*. Photolysis of *26* in the absence of an electron acceptor gave no discernible photochemistry. However, photolysis of *26* in the presence of chlorobenzene (acting as the electron acceptor) gave the product mixture shown in (Eq. 8), which can be rationalized as arising from initial electron transfer from photoexcited *26* to chlorobenzene (an $S_{RN}1$ pathway). Photolysis of *26* in the presence of *trans*-stilbene resulted in isomerization of *trans*-stilbene to *cis*-stilbene and a mechanism of reaction involving initial electron transfer from photoexcited *26* to *trans*-stilbene was favored over several other mechanistic



(6)



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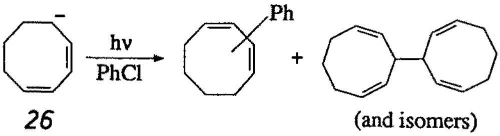
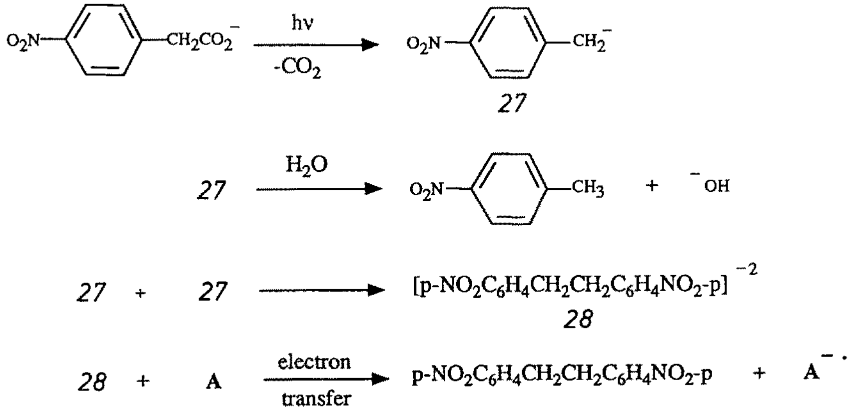


(8)

possibilities [44]. From these examples, it seems clear that there does not exist a simple rule for predicting when electron photoejection will occur in these cyclic carbanions: more exploratory studies are required of these and other carbanions.

1.8 Nitrobenzyl Carbanions

Margerum and coworkers [45, 46] first reported the photogeneration of *m*-and *p*-nitrobenzyl carbanions in aqueous solution from the photodecarboxylation of the corresponding nitrophenylacetate ions. Craig and coworkers [47–49] have studied the kinetics of the photodecarboxylation of *p*-nitrophenylacetate in detail using both picosecond and nanosecond flash photolysis. These above studies have shown conclusively – by direct optical detection of the anion – that the *p*-nitrobenzyl carbanion (*27*) is an intermediate in the photodecarboxylation of the *p*-nitrophenylacetate ion. Wan and Muralidharan [50–52] have shown based on product studies that both the *m*- and *p*-nitrobenzyl carbanions may be photogenerated from a variety of related nitrobenzyl systems, by a relatively general photoretroaldol type reaction. With regards to electron transfer processes of these photogenerated anions, reports of ESR spectra of radical anions of substrate or product nitroaromatics on photolysis of several of the above systems have appeared [48, 52]. These observations along with product [50, 51] and kinetic [48, 49] studies indicate that the electron transfer step takes place from the *p,p′*-dinitrobibenzyl dianion (*28*) intermediate (Scheme 8), to an electron acceptor A in the system



Scheme 8

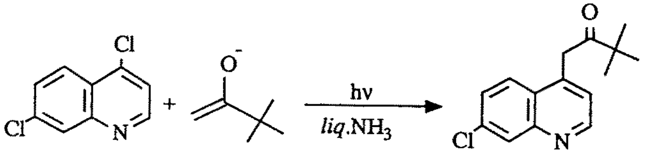
(typically the substrate or product nitroaromatic, but can also be an added nitroaromatic electron acceptor). The *p,p′*-dinitrobibenzyl dianion (*28*) is formed from dimerization of photogenerated *p*-nitrobenzyl anion (*27*) (Scheme 8). Protonation of *27* by water is a competing but relatively slow process ($k = 1.3 \times 10^{-2}\ s^{-1}$). The decay pathways open for $A^{-\cdot}$ are unknown at this time.

1.9 The $S_{RN}1$ Reaction

Perhaps the most common use of carbanions in organic photochemistry is in the synthetically useful $S_{RN}1$ reaction. The reaction proceeds via a radical chain mechanism, which requires the transfer of an electron in an initiation step. Photoinduced electron transfer from a carbanion, which also serves as the nucleophile, is a convenient and mild method of initiation. A generalized mechanism is shown in Scheme 9. The excited state anion, with its enhanced reducing power, transfers an electron to the substrate in the initiation step (1). After fragmentation of the radical anion in step (2), a new carbon-carbon bond is formed via the coupling of a free radical with the anion in step (3). The cycle is propagated when the radical anion of the product undergoes electron transfer with another acceptor molecule in step (4). Originally, the reaction was employed to generate α-aryl ketones, by using enolates as the anion source and aryl halides as the acceptor substrates. Recently, the reaction has gained in both scope and versatility by employing a host of other anions and a wide variety of electron acceptors. In addition to extending the reaction to new substrates, work has been carried out on various structure-reactivity dependences, and regiochemical aspects of new substrate-nucleophile combinations. A full discussion of the advances in the $S_{RN}1$ reaction are beyond the scope of this review. The reader is therefore referred to earlier reviews of this topic [16, 53–56] and references cited therein. Recently, Galli [57] has carried out a study on the effect of substrate structure on the overall reactivity in $S_{RN}1$ reactions. In studying the series of aryl bromides (phenyl, 3-thiophenenyl, 4-biphenyl, 2-pyridyl, 1-naphthyl, and 9-anthryl) he found that the overall reactivity was dominated by ease of formation of the radical anion. This is true even though the rates of radical anion fragmentation have been determined to be in the opposite order [58]. Wolfe and coworkers [59–62] have carried out a great deal of work extending the $S_{RN}1$ reaction to a variety of

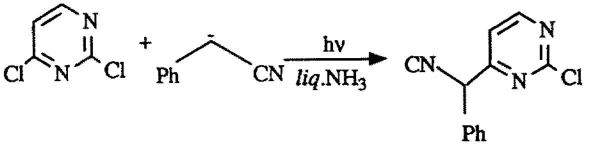
$$
\begin{array}{rcll}
R^- & \xrightarrow{h\nu} & (R^-)^* & \\
(R^-)^* + A\text{-}X & \longrightarrow & R\cdot + A\text{-}X^{-\cdot} & (1) \\
A\text{-}X^{-\cdot} & \longrightarrow & A\cdot + X^- & (2) \\
A\cdot + R^- & \longrightarrow & A\text{-}R^{-\cdot} & (3) \\
A\text{-}R^{-\cdot} + A\text{-}X & \longrightarrow & A\text{-}R + A\text{-}X^{-\cdot} & (4)
\end{array}
$$

Scheme 9



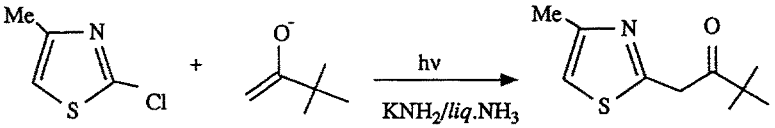
(9)

new substrates. The photo-assisted electron transfer from pinacolone enolate to dihalopyridines resulted in moderate to good yields of the substitution products [59]. A variety of other heterocycles, both π-deficient and π-excessive, have also been demonstrated to act as good substrates [60, 61]. The reactions are typically regiospecific as the following examples illustrate, Eq. 9–11. In an analogous fashion the enolates of *N*-acyl-o-chloroanilines and *N*-acyl-o-chlorobenzylamines have been used in the photoinduced cyclization reactions to afford various alkyloxindoles and 1,4-dihydro-3(2*H*)-isoquinolines, in moderate to excellent yields [62] (Eq. 12). The proposed mechanism involves an intermolecular electron transfer to the aryl moiety, followed by fragmentation of the aryl-halide bond and then ring closure of the resulting radical anion. The choice of solvent or the nature of the counter ion can have major effects on the outcome of the reaction. For instance, Wolfe and coworkers [62] have found that LDA in THF was the preferred base-solvent system for some photocyclizations while KNH_2 in liquid NH_3 gave better results for other substrate-nucleophile combinations. Although, the origins of these effects are not clearly understood, the reduction potential of the counter ion and the extent of solvation are expected to have dramatic effects on the energetics of electron transfer between charged species. A number of other substrates have served as acceptors in the $S_{RN}1$ reaction. Rossi [63] has used



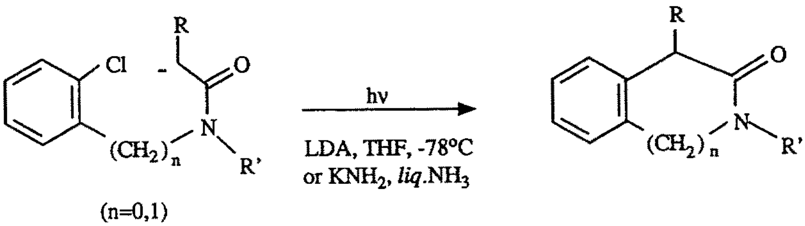
(10)

58% ref. 59



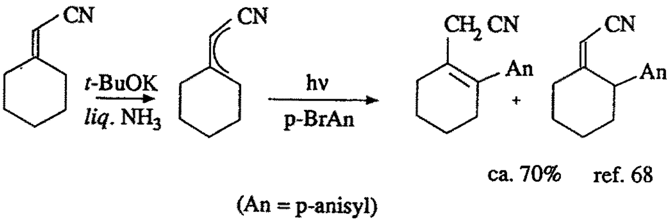
(11)

64% ref. 61



(12)

haloadamantanes and both Rossi [64] and Meijs [65] have reported on the use of 7-bromonorcaranes. Although the photoinduced electron transfer step still occurs, most carbanionic nucleophiles serve only as reducing agents, yielding the dehalogenated substrates rather than the substitution products. Other anions, such as diphenylphosphide, gave good yields of the substitution products. Feiring [66] and others [67] have reported on the use of perfluoroalkyl iodides as substrates. Rossi [68] has investigated the use of various acetonitrile derivatives as carbanion sources. He has recently reported that exocyclic α,β-unsaturated nitriles provide a new route to C-arylation of aliphatic rings. When cyclohexenylideneacetonitrile was subjected to $S_{RN}1$ conditions, only C_γ arylation was observed (Eq. 13).

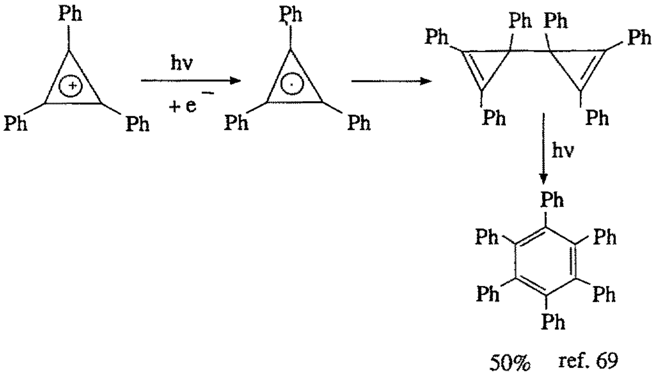


(13)

2 Photoinduced Electron Transfer Reactions of Carbocations

Interestingly, the photochemistry of carbocations has remained comparatively unexplored. The number of reports of photoinduced electron transfer to carbocations is very limited. Radical cations are more familiar in organic photochemistry and electron transfer reactions often play an important role in their mechanistic pathways. This topic is treated separately in chapters 1.5 and 1.6 of this monograph. It is well known that neutral molecules become better electron acceptors and donors in the excited state. Carbocations, which are electron deficient to begin with, are anticipated to be particularly good electron acceptors following photoexcitation. Carbocations and their charge transfer complexes absorb longer wavelength light than their covalent counterparts. While this makes them attractive for visible light induced photochemistry, it may limit their utility since less energy is made available for chemical transformations. Although some researchers have recently employed carbocations as electron acceptors in PET reactions, much of this preliminary work has concentrated on the investigation of mechanism, rather than synthetic utility.

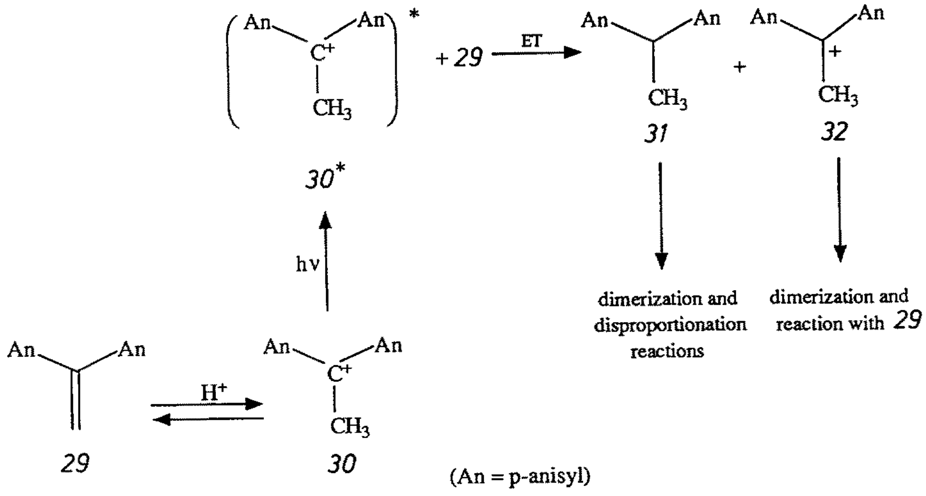
In the early 1970s, van Tamelen and co-workers reported on the steady state photolysis of several stabilized carbocations [69–72]. The reactions were often complex, and very dependent on the solvent conditions. Although no electron donors were deliberately added, the nature of the products occasionally suggested an electron transfer process had taken place. For instance, when triphenylcyclopropenium bromide was photolyzed in 10% aqueous sulfuric acid solution, hexaphenylbenzene was isolated in 50% yield (Eq. 14). The reaction efficiency increased substantially when methanol was added as a cosolvent. The source of the reducing electrons was not specified.



(14)

2.1 Diarylmethyl Cation

A photoinduced electron transfer mechanism has been proposed by de Mayo and coworkers to explain the products arising from the irradiation of 1,1-di-*p*-anisylethene in benzene-trifluoroacetic acid solutions [73]. Photolysis (>430 nm) of the (di-*p*-anisylmethyl)methyl cation *30* resulted in electron transfer from the neutral substrate *29* as shown in the Scheme 10. No reaction occurred under these conditions in the absence of acid. The quantum yields of the photoproducts are



Scheme 10

very low ($\simeq$ 0.001) presumably a result of an efficient back electron transfer process [73]. The nature of the final products provided strong evidence for the intermediacy of the radical *31* and the radical cation *32*. When a better electron donor such as 1,2,4-trimethoxybenzene (TMB) was added, it intercepted the excited state cation *30** resulting in a decrease in the products arising from the radical cation *32*. Furthermore, the presence of TMB quenched the dimerization of *31*, indicating that the back electron transfer reaction is more facile with TMB than with *29*. Direct observation of the radical cation *32* has been accomplished using microsecond flash photoylsis techniques. Using dicyanoanthracene as the excited state electron acceptor in the presence of *29* resulted in the same transient absorption assigned to *32*. Furthermore, when TMB was added this transient was completely quenched.

2.2 Tropylium Cation

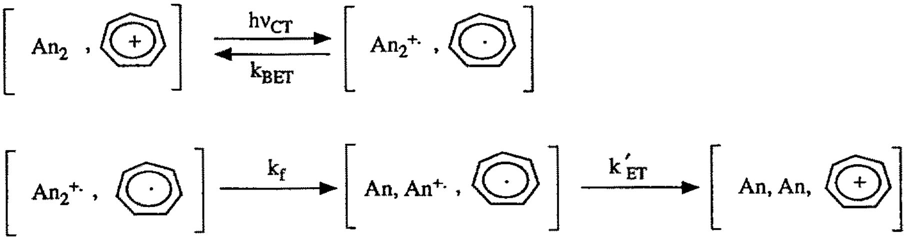
Kochi and co-workers have recently identified and characterized the weak charge transfer complexes between tropylium ion and a series of substituted arenes in acetonitrile solution [74]. Photoexcitation of these electron donor acceptor (EDA) complexes leads to an electron transfer from the arene donors to the tropylium ion in accord with Mulliken's theory [75]. Time resolved spectroscopic observation of the arene radical cations (formation within the 30 ps laser pulse) has confirmed their intermediacy. The subsequent decay of the photogenerated radical cation and the concomitant regeneration of the ground state EDA complex occurs with a rate constant, $k_{BET} > 4 \times 10^{10}\ s^{-1}$ (Scheme 11). This fast back electron transfer reaction competes with diffusive separation or bimolecular processes. (i.e., photochemical transformations resulting from charge transfer (CT) excitation are limited by the lifetime of the arene radical ion, $\tau \simeq 15$ ps) [74]. Hence, prolonged photolysis of the charge transfer complexes of substituted benzenes, naphthalenes, and anthracenes failed to yield any detectable photoproducts. Even in the presence of nucleophiles (such as acetic acid or methanol) and hindered bases (such as 2,4,6-collidine) no net photochemistry or change in the transient behaviour was observed. Unimolecular processes, however, can be quite rapid and hence may compete with back electron transfer. In the same article, the authors report that the charge transfer cycloreversion of dianthracene occurs with a quantum yield of 0.02. The unimolecular fragmentation rate of the dianthracene radical cation was independently estimated at $k_f \simeq 10^8\ s^{-1}$ [76]. Fragmentation only marginally competes with the back electron transfer, resulting in the low photoefficiency of

$$\mathrm{Ar} + \mathrm{Trop}^{+} \underset{K < 1\,M^{-1}}{\overset{K}{\rightleftharpoons}} [\mathrm{Ar}, \mathrm{Trop}^{+}] \underset{k_{BET}}{\overset{h\nu_{CT}}{\rightleftharpoons}} [\mathrm{Ar}^{+\cdot}, \mathrm{Trop}^{\cdot}]$$

(Ar = substituted benzenes, napthalenes, anthracenes)

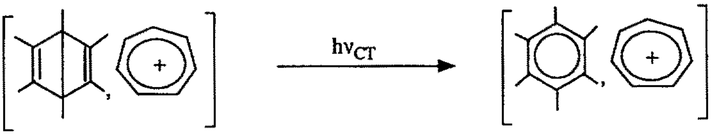
Scheme 11

this process (Scheme 12). The isomerization of hexamethyl Dewar benzene was similarly photoinduced via charge transfer excitation (Eq. 15). Estimates of the quantum yield are greater than unity [74] reminiscent of earlier investigations of this isomerization [77, 78]. A radical cation chain mechanism could explain how a minor pathway, competing with back electron transfer, could become magnified [74].



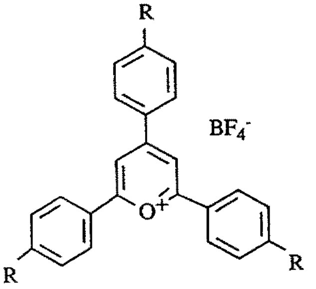
(An_2= head to tail 9,10 dimer of 9-methylanthracene)

Scheme 12

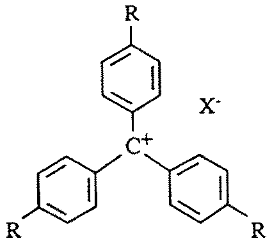
 (15)

2.3 Pyrylium and Trityl Cations

In connection with solar energy storage investigations, Mukai and co-workers reported on the use of cationic sensitizers *33–37* in the photocycloreversion reaction of strained molecules [79, 80] (Eq. 16). Acetonitrile solutions of the

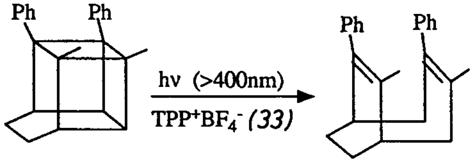


33 R=H
34 R=OMe



35 R=H X⁻=BF_4^-
36 R=OMe X⁻=Cl⁻
37 R=OMe X⁻=BF_4^-

substrate and sensitizer ($TPP^+BF_4^-$ = triphenylpyrylium tetrafluoroborate *33*; approx. 10% mole equivalent) were irradiated with visible light. For the reaction of *38* chemical yields ranged from 60 to 100%, and quantum yields up to about 80% were obtained depending on the sensitizer used. A radical chain mechanism (via a photoinduced electron transfer) has been proposed for the process [80] (Scheme 13). The electron transfer step was supported by the following observations: (1) quenching of the sensitizer fluorescence followed Rehm-Weller behaviour, with $k_q\tau$ increasing to a constant value as the oxidization potential of the quencher decreased; (2) the cycloreversion of *38* was efficiently quenched by the addition of the electron donor tetramethoxybenzene. The authors propose that the excited singlet state of the cation acts as the electron acceptor [80]. Changing the counterion from tetrafluoroborate to chloride, *36* and *37* above, resulted in a dramatic decrease in the quantum yield of *39*. The oxidation potentials of these salts, ($E^{ox}_{1/2}$ = 2.0V and 1.0V vs. SCE, respectively), suggest that intramolecular electron transfer from the chloride ion competes favorably with the productive intermolecular electron transfer step [79]. In 1987 Akaba and coworkers [81] described the use of $TPP^+BF_4^-$ (*33*) to sensitize an electron transfer oxygenation reaction. Irradiation of the adamantylideneadmantane through a Pyrex filter in oxygen saturated dichloromethane gave the corresponding dioxetane in 78% yield. The transient absorption observed after a nanosecond laser flash was assigned to the TPP$^·$ radical and was used as direct evidence of photoinduced electron transfer to the excited singlet state of TPP^+ from the alkene.



(38) (39)

(16)

$$\left.\begin{array}{l} \mathrm{Sen}^+ \xrightarrow{h\nu} {}^1(\mathrm{Sen}^+)^* \\ {}^1(\mathrm{Sen}^+)^* \longrightarrow \mathrm{Sen}^+ \\ {}^1(\mathrm{Sen}^+)^* + 38 \longrightarrow \mathrm{Sen}^{\cdot} + 38^{+\cdot} \end{array}\right\}\ \text{initiation}$$

$$\left.\begin{array}{l} 38^{+\cdot} \longrightarrow 39^{+\cdot} \\ 39^{+\cdot} + 38 \longrightarrow 39 + 38^{+\cdot} \end{array}\right\}\ \text{propagation}$$

$$\left.\begin{array}{l} \mathrm{Sen}^{\cdot} + 38^{+\cdot} \longrightarrow \mathrm{Sen}^+ + 38 \\ \mathrm{Sen}^{\cdot} + 39^{+\cdot} \longrightarrow \mathrm{Sen}^+ + 39 \end{array}\right\}\ \text{termination}$$

Scheme 13

3 Summary

The low energy transitions associated with charged organic substrates make them attractive in organic photochemistry. Photoinduced electron transfer can, in principle, be selectively carried out without interference from energy-transfer processes or other photochemical reactions. Nonetheless, the ubiquitous back electron transfer reaction continues to be an impediment in a number of the examples cited. It is worth mentioning, that the choice of solvent and counterion can be crucial in determing the efficiency and even the course of the reaction.

It is clear from this review that the topic of photoinduced electron transfer from carbanions is well-developed, with important synthetic applications, as exemplified by the $S_{RN}1$ reactions. There is sufficient data available to indicate that electron transfer from photoexcited carbanions is a reasonably general process. It is now possible to predict with some certainty which systems will undergo PET. This area will see continued development especially with respect to the details of reaction. Much less is known with respect to PET to carbocations. However, it is clear that this is a developing area and the examples presented provide us with new opportunities for exploratory studies. Whereas neutral molecules have been traditional substrates for PET studies in the past, it is clear that both carbanions and carbocation can also serve as substrates for such investigations, which may lead to interesting results.

4 Acknowledgment

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Additional support was provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada in the form of an operating grant and a post-graduate scholarship (to E.K.).

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Photoinduced Electron Transfer Oxygenations

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The fundamental work of Weller and co-workers on the dynamic fluorescence quenching of singlet excited states of electron acceptors by donors with the generation of free radical ions and the Marcus treatment of these processes, that attempted to bring order into organic electron-transfer chemistry, can be considered as basic studies that, in the late '70s, gave the impulse to the development of the photoinduced electron-transfer oxygenation of several classes of organic compounds as a useful synthetic tool in peroxide chemistry. The enormous

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interest of this new mode of oxygen functionalization, that can be applied either to reactive substrates towards singlet oxygen or to those totally inert versus this intriguing electronic excited state of molecular oxygen, has been documented by numerous publications on this topic.

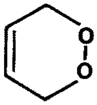
After a brief introduction on the singlet oxygenation, the first and more studied procedure of oxygen functionalization of unsaturated organic compounds, it shall be tried to present a brief overview of the theoretical work and of the sophisticated analytical techniques that support and permit the detection and characterization of the elusive radical ions involved in the P.E.T-oxygenation procedure. Following a short mechanistic orientation on the original Foote's proposal, there will be detailed, in relation to the peculiar physical properties of the sensitizers and organic compounds, the actual different mechanisms that can operate in these processes and how they can be controlled or modified upon the addition of inert reagents such as salts, aromatic hydrocarbons, quinones, and amines. From the synthetic point of view, this critical analysis appears of fundamental importance. In fact, although this area has been extensively reviewed in the last years, its potential as a synthetic tool in peroxide chemistry has not yet been stressed. In this regard, the search for new nonconventional sensitizers together with a simultaneous growing interest in organic syntheses that proceed via electron-transfer processes should greatly help in this effort.

1 Introduction

Photoinduced oxygenations of unsaturated and heterocyclic organic compounds have long been considered to proceed via energy-transfer quenching of a large number of $n\pi^*$ and $\pi\pi^*$ triplet-excited sensitizers by molecular oxygen with the concerted or stepwise electron-exchange generation of singlet oxygen ($^1O_2$) as the reactive intermediate [1, 2].

When in the early 60s it was demonstrated that this intriguing electronic excited state of molecular oxygen ($^1\Delta$) – since the 30s suggested by Kautsky as key intermediate in the dye-photosensitized oxidation of organic substrates [3] – could be prepared chemically [4–11] and by microwave discharge [12–16], its physical, chemical, and biological aspects were extensively studied in interdisciplinary subdisciplines.

In spite of the rather great variety of singlet oxygen sources available for laboratory purposes, significant synthetic progress in peroxide chemistry [17–20] was achieved in the 70s with the syntheses of new insoluble polymer-bound sensitizers [21], exchange resins forming very strongly bound complexes with ionic sensitizers [22], or adsorbant-bound heterogeneous photosensitizers [23] that, avoiding all the inconvenciences of the homogeneous photooxygenation, turned this procedure into a particularly useful synthetic tool. The $^1\Delta$ state of molecular oxygen, isoelectronic with ethylene in view of its electrophilic character [24–26], plays the role of a dienophile vs unsaturated organic compounds leading to the facile synthesis of endoperoxides *1*, allylic hydroperoxides *2* and, above all of 1,2-dioxetanes *3*, "high energy molecules" via 1,4-, 1,3-, 1,2-cycloaddition reactions.



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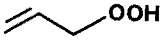

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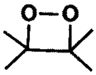

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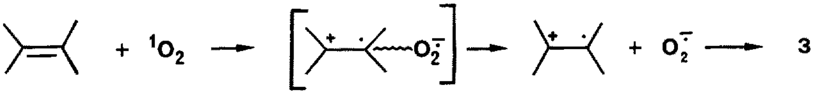
The great synthetic value of these simple and elegant procedures of introducing the peroxide linkage into organic substrates, together with their involvement as plausible intermediates in biological oxidations [27, 28] and their promising medical applications [29–31], justify the important amount of work that has been devoted to the singlet oxygenation of several classes of organic substrates over the past 30 years.

However, in recent years, it has become apparent that several photoinduced oxidation reactions do not involve singlet oxygen as the reactive intermediate, and, consequently, the reaction products cannot be accounted for the mechanisms shortly reported above. Moreover, since the first report on the photochemical stereospecific synthesis of the most fascinating peroxide derivatives, i.e., 1,2-dioxetanes [32], it clearly appeared, with a few notable exceptions [33, 38], that only electron-rich olefins, such as enamines, enol ethers, and thio-substituted olefins, characterized by low one-electron oxidation potentials, could undergo an easy singlet oxygen functionalization [17–20].

Among the suggestions for the [2 + 2] cycloaddition mechanism of $^1O_2$ to olefins, Foote et al. [39, 40] proposed a nonconcerted pathway involving a rate-limiting electron-transfer process with the formation of an olefin radical cation and superoxide ion complex (Scheme 1).



Scheme 1

The reported stereospecific dioxetane formation [32] would rule out an electron-transfer process since it must produce an open radical cation with consequent bond rotation and loss of the configuration. However, additional theoretical and experimental evidence suggest that this process might play an important role in the primary step of the oxidation of highly electron-rich substrates. Basically, singlet oxygen can be more susceptible to one-electron-transfer with electron donors than triplet oxygen since excitation of molecular oxygen to $^1O_2$ results in an increase in the one-electron reduction potential by 1 eV. One-electron-transfer mechanisms have therefore been postulated in the cycloadditions of $^1O_2$ to enamines [39, 40], in the reactions with phenols [41, 42], sulfides [43], azines [44], amines [45–47], as well as with mitochondrial components such as NADH and reduced cytochrome *c* [48]. Anyway, direct observation of the proposed oxygen radical/ion-radical cation complex may prove difficult since the complex might well decay to the dioxetane within the solvent cage, thus putting the time scale of the decay in the subnanosecond region [49]. Furthermore, Schaap et al. [50], in a detailed kinetic study on singlet oxygenations of activated olefins (enol ethers), reported clear experimental data militating against the radical and zwitterionic mechanisms. Although Schaap limited the mechanistic possibilities for the cycloaddition of singlet oxygen to activated olefins, these first attempts to re-evaluate this mechanism in terms of one-electron-transfer process can be considered as a natural consequence of the mechanistic ferment, started in the 40s, that has left few organic reactions untouched from the mechanistic point of view [51, 52].

In fact, in the early years of physical organic chemistry, mechanisms involving radical ions did not enjoy much acceptance, remaining of interest in a narrow circle of specialists [53–57].

As stated by Eberson [51], modern organic electrochemistry [58] and the development of photoorganic chemistry, being exceedingly rich sources of organic electron-transfer phenomena, have changed this *state of affair*.

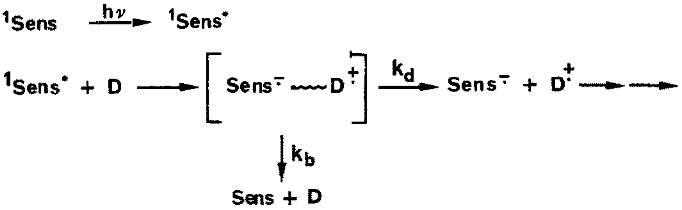
The main scientific achievements that during the 70s have given the impulse to the development of photosensitized electron-transfer reactions, in particular to the photoinduced electron-transfer oxygenation of several classes of organic substrates, have been: (a) the codification of a still increasing number of unsaturated and heterocyclic organic substrates totally inert vs singlet oxygen; (b) the pioneering work of Weller [59], Cohen [60], and their co-workers on the fluorescence quenching of singlet excited electron acceptor (A or Sens) by donors (D) via one-electron transfer mechanisms; (c) the development of a new generation of laser flash spectroscopic [61, 62], conductometric, and magnetic [63–65] techniques to identify and study other types of intermediates, which might play a role in electron transfer processes; (d) the studies of Marcus [66], Shaik [67], and Pross [68] on electron-transfer reactions.

Our objective in this article will be to select critical examples dealing with the photooxygenation of organic substrates, in which experimental evidence strongly support a photochemically initiated electron-transfer mechanism, thus opening an entirely new perspective in peroxide chemistry. Our aim will be also to introduce the interested reader to mechanistic features which must be dealt with in investigating photoinduced transformations. On the other hand, because this area is inherently interdisciplinary, it is rather hard to provide a detailed compilation of all work relevant to the photoinduced reactions of concern. Thus, except for few cases, no attempt will be made to discuss the diversified chemistry of photosensitized electron-transfer processes, extensively reported in several excellent reviews [69–72].

2 Preliminary Hypotheses and Experimental Evidence for Electron Transfer

Since the pioneering work of Weller [59], fluorescence quenching of excited states via one-electron-transfer mechanism has been a subject of great interest among photochemists and photophysicists [73]. Quenching by electron transfer is one electron-transfer reaction in which an electron jumps from an occupied molecular orbital of one reactant to an unoccupied molecular orbital of the other. Thus, an excited-state molecule (triplet or singlet depending on its multiplicity), due to the double character of a radical cation (half-filled HOMO) and of a radical anion (half-filled LUMO), can exert oxidizing properties towards a donor and reducing properties towards an acceptor with the generation of a radical ion pair. However, in this elementary process, where bonds are neither broken nor formed, the transfer of an electron between uncharged species, occurring under extremely mild conditions, induces a drastic change of their chemical reactivity. For example, nucleophilic reagents are transformed by loss of an electron into electrophiles. Vice versa the reduction of electrophilic reagents enhance their nucleophilic character. The sensitizer's excited state can be an electron donor or acceptor and, in any case, an electron-transfer process between uncharged species leads to a radical ion pair [2, 72, 74].

An adequate description of the exchange of an electron between two chemical substrates must take into account the positions and motions of the reactants in a given molecular environment. The two free species diffusing in the medium, may form a precursor complex, also denoted as collision or encounter complex. An encounter complex can be envisaged as an intermolecular ensemble of an excited-state and ground-state molecule separated by a small distance and surrounded by solvent molecules. During the lifetime of an encounter complex, the reactants undergo structural and electronic changes. If the transfer of an electron occurs within this lifetime, the charge-transfer species immediately leads to a contact ion pair, which, depending on solvent polarity, may afford solvent separated ion pair and then free radical ions. On the other hand, if the interaction between the electronically excited and ground-state molecules is particularly strong, the encounter complex may rapidly form a new intermediate, which may have a sufficiently long lifetime to undergo a red-shifted light emission. Such intermediates are termed exciplexes and are characterized by strong binding energies (5–20 kcal/mol), partial charge character, and large dipole moment. A number of excellent reviews and books with all the references on this topic can be consulted for more details (see for example Refs. [2, 72, 74]). Anyway, most work in photoinduced electron-transfer oxygenation has been centered around the electron transfer to the singlet excited state of fluorescing aromatic molecules (Sens) in the presence of electron-donors (D). Thus, the reaction is accompanied by fluorescence quenching of the light absorbing molecule (Scheme 2).



Scheme 2

The produced radical ions, in virtue of their dual functionality: ionic and radical, may back transfer the electron to restore Sens and D ground states or may go on to produce several new reaction products in relation to the reaction conditions [69–72, 75].

The feasibility of a photochemical electron-transfer reaction between an excited-state sensitizer and a quencher is dictated by the overall change in free energy ΔG which accompanies the reaction. In polar solvents, it can be predicted on the basis of the simple equation derived by Weller and co-workers [59]:

$$\Delta G\ (\text{Kcal/mol}) = 23.06[E_{D/D^{+\cdot}} - E_{\text{Sens}^{-\cdot}/\text{Sens}} - e_0^2/a\varepsilon] - \Delta E_{O-O} \qquad (1)$$

in which $E_{D/D^{+\cdot}}$ and $E_{\text{Sens}^{-\cdot}\text{Sens}}$ are the electrochemically determined oxidation and reduction potentials for the donor and sensitizer, respectively, measured in volts; $e_0^2/\varepsilon a$ is the energy gained by bringing the two radical ions to the encounter distance a in a solvent of dielectric constant ε (0.06 eV in acetonitrile), and ΔE_{O-O} is the electronic excitation energy of the O – O transition of the sensitizer. In other words, it claims that when the excitation energy (singlet or triplet, reflecting that of the excited molecule involved in the reaction) exceeds the energy stored in the pair by a few kilocalories per mole, the electron-transfer reaction proceeds at diffusion-controlled rate.

Quenching of the fluorescence of singlet excited electron-acceptor molecules can also be measured in nitrogen-saturated polar solvent by using the Stern-Volmer equation [76]:

$$I_0/I_q = 1 + k_q\tau[D] \tag{2}$$

where I_0 and I_q are relative fluorescence intensities in the absence and presence of the donor [D], τ is the lifetime of the singlet excited state of the fluorescer [15.3 ± 0.1 ns for DCA] [77]. Plots of I_0/I_q vs the concentration of the quencher provide values for $k_q\tau$, from which quenching rate constants k_q (ca. $10^{10}\ M^{-1}\ s^{-1}$) are calculated (Table 1).

Table 1. DCA-Fluorescence Quenching Rates (Kq); E^{ox}(D), and calculated ΔG for E.T.[a]

Sensitizer[b]	Donor	Kq ($10^{10}\ M^{-1}\ s^{-1}$)	E^{ox} (V)[c]	ΔG (Kcal/mol)[d]
DCA	Biphenyl	0.30	1.91[e]	− 1.4
DCA	Mesitylene	0.05	1.90[e]	− 1.5
DCA	Anisole	1.22	1.76[d]	− 4.8
DCA	1,1-Diphenyl ethylene	0.85	1.52[f]	−10.4
DCA	Trans-Stilbene	1.88	1.51[f]	−10.6
DCA	Tetraphenylethylene	1.78	1.33[f]	−14.8
DCA	1,2,4-Trimethoxybenzene	1.83	1.12[g]	−19.6

[a] In acetonitrile; [b] 9,10-dicyanoanthracene see test; [c] in acetonitrile except as noted; [d] calculated from Weller's equation see Ref. [59]; [e] see Ref. [78]; [f] see test; [g] see Ref. [79]

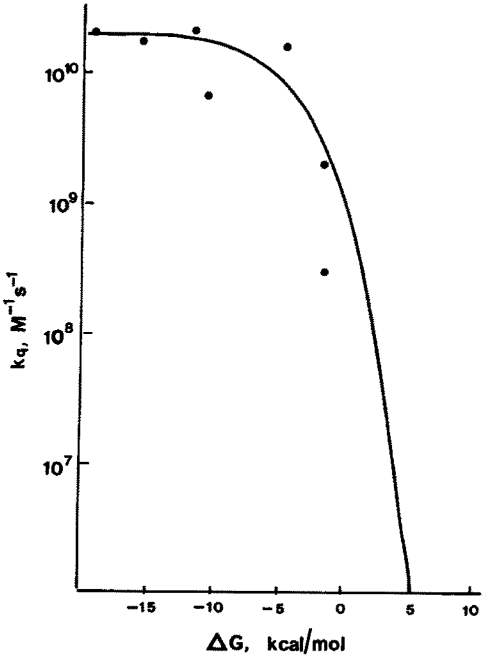


Fig. 1. Plot of rate constant for fluorescence quenching k_q vs free energy ΔG for E.T. The *solid line* is calculated by Rehm and Weller for an E.T. process

A plot of k_q *vs* ΔG can give a good correlation with the theoretical line calculated by Rehm and Weller [59] for an electron-transfer process (Fig. 1).

However, the most common reaction of the primary geminate radical ion pair is the back-transfer of an electron leading to the singlet ground state reactants or to the triplet state of one of the reactants in relation to the multiplicity of the pair and to the energy stored in the pair [80]. Low viscosity and high polarity of the medium reduce the former unlikely process. Mattes and Farid [81], Mataga [82], Farid and Gould [83] have shown that the quantum yield for solvent-separated radical ions in electron-transfer fluorescence quenching is a function of the exothermicity of the back electron-transfer process from the electron acceptor radical anion to the donor radical cation:

$$\begin{gathered} {}^{1}\left[\mathrm{DCA}^{\overline{\cdot}} \sim\sim \mathrm{D}^{\dot{+}}\right] \xrightarrow{k_b} \mathrm{DCA} + \mathrm{D} \\ \Delta G_b = \left[E^{red} - E^{ox}\right] \end{gathered} \tag{3}$$

For example, with the same singlet-excited sensitizer, i.e., 9,10-dicyanoanthracene DCA [$E^{red} = -0.89$ V vs SCE; $\Delta E_{O-O} = 2.94$ eV] [84] and two different electron donors, the quantum yield for the formation of separated radical ions increases from 0.03 to 0.3 as the exothermicity for back electron-transfer, in relation to the donor's oxidation potentials, increases from 2.1 to 2.8 eV.

In other words, the rate constant k_b [see Eq. (3)] for this singlet recombination is thought to decrease as the exothermicity increases. We will stress this concept in a subsequent section, i.e., in the indirect and modified DCA-sensitized photooxygenations of several organic compounds.

The back electron-transfer in a triplet geminate pair seems strictly related to the triplet energy of one of the reactants. In fact, if one of them has a triplet energy (E_T) lower than the energy stored in the pair [85], the exergonic process [Eq. (4)] will be significant [86]:

$$\begin{gathered} {}^{3}\left[\mathrm{Sens}^{\overline{\cdot}} \sim\sim \mathrm{D}^{\dot{+}}\right] \longrightarrow {}^{3}\mathrm{Sens}^{*} + \mathrm{D} \quad \text{or} \quad \mathrm{Sens} + {}^{3}\mathrm{D}^{*} \\ \Delta G = \left[(E_T) - (E^{ox} - E^{red})\right] \end{gathered} \tag{4}$$

Otherwise, different processes (separation, spin inversion, etc.) will occur. In fact, it is possible that several chemical processes take place within the cage, i.e., proton transfer or interception of the geminate pair. Reactions of neutral olefins or alkynes with their corresponding radical cations, while still in cage with the radical anions, are likely to compete with other processes of the geminate pair expecially if a high concentration of the reactants are present in the medium [87]. The resultant dimeric radical cations, being still in cage with the radical anion, are likely to be efficiently reduced to the corresponding biradicals through a reverse electron-transfer process as shown in Eq. (5):

$$\left[\text{Sens}^{\overset{-}{\cdot}} / \overset{+}{\text{D}}\!\sim\!\text{D}^{\cdot}\right] \longrightarrow \text{Sens} + {}^{\cdot}\text{D—D}^{\cdot} \tag{5}$$

Therefore, the main aim in all the photosensitized electron-transfer reactions, including oxygenations, is to prolong the lifetime of the intermediate radical ions maximizing their cage escape efficiency, such that the dark chemistry of the oxidized and/or reduced species can be more easily controlled.

In most of the photoinduced electron-transfer oxygenations discussed in this article, the radical cations are produced: (1) by reaction of donors with excited electron acceptors; (2) by secondary electron-transfer processes through reactions of donors with a primary radical cation. Electrode-catalyzed, and/or thermally induced formation of radical cations will be also introduced, in order to discuss and elucidate the actual mechanisms operating in several photoinduced electron-transfer oxygenations. Some of the more commonly used light-absorbing electron-acceptors which function as sensitizers for the formation of substrate radical cations $D^{\dot{+}}$, are listed in the Table 2 together with the excitation energy (O – O transition of the fluorescence spectrum) in eV and the corresponding reduction potential in Volts. Meanwhile, the oxidation potentials of each one of the electron-rich organic substrates, in part reported in Table 1, will be indicated.

Table 2. Reduction Potentials and Excitation Energy of Some Electron Acceptors[a]

Sens	Reduction Potential E^{red} V vs SCE CH_3CN	Excitation Energy $^1(E_{O-O})^*$ eV
Trityl tetrafluoroborate (TPC^+ $BF4^-$)	0.29[88,89]	
2,4,4,6-tetrabromocyclo hexa-2,5-dien 1-one (TBCHD)	0.26[90]	2.94
2,3,5,6-tetrachloro-p-benzoquinone (TBC)	0.02[91]	
2,4,6-triphenylpyrylium Tetrafluoroborate (TPP^+ $BF4^-$)	−0.29[88,89]	2.8
2,6,9,10-tetracyanoanthracene (TCA)	−0.45	2.82
1,2,4,5-tetracyanobenzene (TCB)	−0.65	3.83
9,10-dicyanoanthracene (DCA)	−0.89	2.88
1,4-dicyanonaphtalene (DCN)	−1.28	3.45
1-cyanonaphtalene (1-CN)	−1.98[92]	3.75
2-cyanonaphtalene (2-CN)	−2.13[92]	3.68

[a] Unless otherwise indicated the values reported in the table are from Refs. [71, 84, 95]

In relation to the reduction potentials and to the energy of the singlet excited state of electron acceptors, we can set, applying Weller's equation, the maximum oxidation potential of electron donors to efficiently quench the fluorescence of each one of the electron acceptors listed above. In other words, with the most commonly used electron acceptor, DCA, its fluorescence will be efficiently quenched only by donors with oxidation potentials lower than 2 V vs SCE (calomel standard electrode). Instead, with 2,6,9,10-tetracyanoanthracene (TCA), which has a singlet energy similar to that of DCA, but is much easier to reduce, its fluorescence will be quenched by donors with oxidation potentials as great as 2.5 V vs SCE.

From this point of view, in order to generate and study the reactions of radical cations of a still increasing number of organic substrates, a future development of this field will be ensured by the syntheses of new electron acceptors much easier to reduce than those previously listed.

If this aspect is of critical importance in most of photoinduced electron-transfer reactions, it presents, at the same time, important consequences in photoinduced electron-transfer oxygenations, as we will describe in the next section.

3 Photoinduced Electron Transfer Oxygenation of Unsaturated Substrates

In the late 70s, the interest of many groups was aroused by cyanoaromatic compounds (Sens) because they felt that, by proper choice of sensitizer redox potential, the cyanoaromatic radical anions ($\mathrm{Sens}^{\cdot-}$) should be re-oxidized by molecular oxygen to produce, by a second exergonic electron-transfer process, superoxide ion $O_2^{\cdot-}$ [Eq. (6)] [84].

$$\begin{gathered} \mathrm{Sens}^{\cdot-} + {}^3O_2 \longrightarrow {}^1\mathrm{Sens} + O_2^{\cdot-} \\ \Delta G\ (\mathrm{Kcal/mol}) = 23.6\left(E^{red}_{sens} - E^{red}_{O_2}\right) \end{gathered} \tag{6}$$

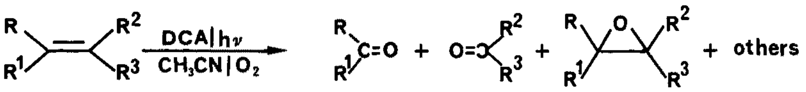
On this ground, DCA was found a suitable sensitizer to induce the photooxygenation of a great variety of organic compounds such as alkenes [84, 94–98], alkynes [99, 100], sulfides [84, 98, 101], dienes [84], sulfoxides [102], cycloalkanes [103, 104], cycloalkenes [105, 106], epoxides [107, 108], aziridines [109], allenes [110], dioxenes [111], *p*-dioxins [111, 112], aromatic substrates [113], tertiary amines [114], and of great interest from the mechanistic point of view, sterically hindered olefines [97, 115–117].

The subsequent reduction of molecular oxygen to superoxide ion is of strategic importance. In fact, it exercises the double function of generating a more reactive oxygen species than molecular oxygen [Eq. (7)], and, at the same time, it avoids

$$D^{\cdot+} + O_2^{\cdot-} \longrightarrow DO_2 \tag{7}$$

or at least reduces the back electron-transfer process [see Eq. (3)] with the regeneration of the ground-state reactants, producing free radical cations.

Thus, Foote and co-workers [84, 94, 95] found that oxygen-saturated acetonitrile solutions of different aryl-substituted olefins 8–11 (2×10^{-2} M) and a proper cyanoaromatic sensitizer, generally DCA (ca. 10^{-4} M), irradiated at wavelengths greater than 400 nm – such that only the sensitizer absorbs light – gave two equivalents of the corresponding carbonyl compounds 12–15. Variable amounts of epoxides 16–19 were also formed along with some minor products [Eq. (8)].



8–11 **12–15** **16–19**

(8)

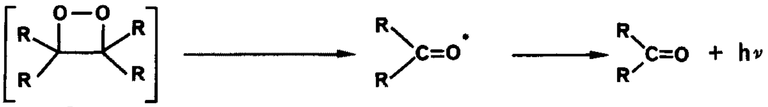
$8\ R = R^1 = R^2 = R^3 = C_6H_5$

$9\ R = R^1 = C_6H_5; \quad R^2 = R^3 = H$

$10a, b\ R = R^3 \text{ or } R^2 = C_6H_5; \quad R^1 = R^2 \text{ or } R^3 = H$

$11\ R = R^1 = p\text{-}CH_3OC_6H_4; \quad R^2 = R^3 = H.$

Carbonyl compounds 12–15 most likely derive from the corresponding intermediate dioxetanes 20, which under the reaction conditions would be expected to decompose thermally and or by direct sensitized photolysis, usually through a chemiluminescent process due to the fluorescence emitted by the singlet electronically excited carbonyl compound [17–20] [Eq. (9)].

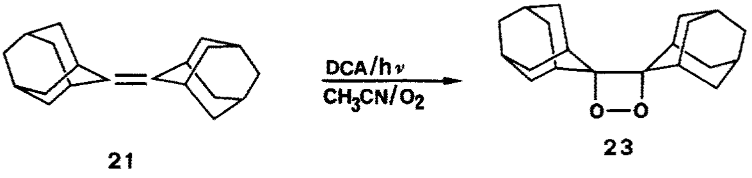


20

(9)

In fact, the chemiluminescence of an authenic sample of *trans*-3,4-diphenyl-1,2-dioxetane, prepared by Kopecky's procedure [118] and then added to the DCA-sensitized reaction on *trans*-stilbene ($E^{ox} = 1.51$ V vs SCE), totally disappears within a few minutes [119]. In spite of this elegant demonstration, the intermediacy of these short-lived compounds required further direct evidence. In this regard, although different mechanistic pathways can account for the reaction products [34, 120, 121], Schaap et al. [98] isolated in the DCA-sensitized photooxygenations of adamantylidene-adamantane ($E^{ox} = 1.46$ V vs SCE) 21 and/or of several substituted 2,3-diphenyl-5,6-dihydro-1,4-dioxins (E^{ox} in the range 0.72–1.07 V vs SCE) 22a–f the correspopnding stable 1,2-dioxetanes 23, 24 a–f [Eqs. (10, 11)] in good yields.

The crystal structure of 23, which has the highest thermal stability among 1,2-dioxetanes, is of particular interest. In fact, it shows a great degree of puckering of the dioxetane ring (ca. 21°) due to the large nonbonding repulsions between



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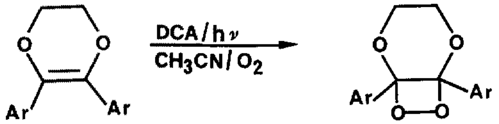
23

(10)



(11)

22a: Ar = C_6H_5; b: Ar = p-$CH_3C_6H_4$; c: Ar = p-$CH_3OC_6H_4$; e: Ar = m-ClC_6H_4; f: Ar = m-$CH_3OC_6H_5$

equatorial hydrogens [122], whereas, for structural necessity, the *p*-dioxin dioxetanes are planar [123]. On the contrary, the route to epoxides, which are minor products in the DCA-sensitized photooxygenation of aryl-olefins, in spite of the hypotheses of Foote et al., is still uncertain [95].

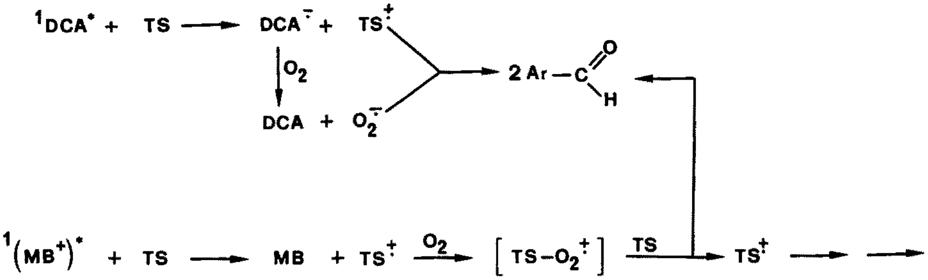
DCA is not consumed in the reaction medium and, for example, no conversion of tetraphenylethylene (E^{ox} = 1.33 V vs SCE) 8 into benzophenone 12 (57%) and tetraphenyloxirane 16 (15%) occurs in the absence of oxygen or in less polar solvents, such as diethyl ether, ethylacetate, carbon tetrachloride, *p*-dioxane, or cyclohexane [84, 95].

More interestingly, no reaction products are formed in an oxygen-saturated acetonitrile solution of 8 containing triplet excitable sensitizers, such as rose bengal (RB) or methylene blue (MB^+), irradiated at $\lambda > 500$ nm. It therefore seems that, in the DCA-sensitized photooxygenation of 8 and similar aryl-olefins, singlet oxygen is not involved at least as reactive intermediate vs the specific substrates [84, 95].

Nearly at the same time, the same group reported a study dealing with the electron-transfer initiated oxidation of *trans*-stilbene (TS) 10a sensitized by the singlet excited states of both $^1DCA^*$ and methylene blue (MB^+) [124]. The authors proposed that, although the initial electron-transfer step was identical for the two systems, the subsequent steps leading to products (predominantly benzaldehyde) must be different. In fact, dicyanoanthracene radical anion $DCA^{\cdot-}$ reduces molecular oxygen to superoxide, whereas reduced methylene blue MB°, owing to its lower redox potential ($E^{red} = -0.25$ V vs SCE), doesn't.

On this ground, they suggested for the two sensitizers the classical Foote proposal for the DCA system [84] and a chain electron-transfer mechanism, like the

Barton-oxidation of dienes for the MB^+ system, in which the oxygen active species is molecular oxygen [125] (Scheme 3).

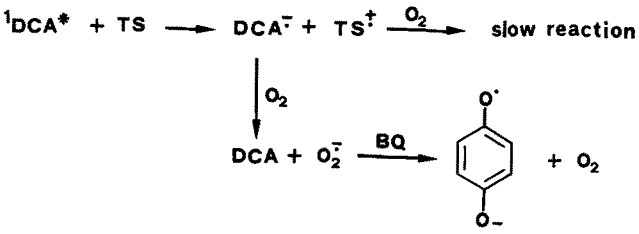


Scheme 3

In the effort to find confirmation on Foote's original mechanistic proposal [84] and discriminate among these two different pathways, a great deal of experimental proofs were achieved. First of all, the DCA and/or 9-cyanoanthracene (CNA)-sensitized reactions on aryl-olefins were studied under inert atmosphere by flash spectroscopic techniques obtaining clear evidence for the formation of both olefin radical cations and cyanoaromatic radical anions [95]. In the presence of oxygen, the cyanoaromatic radical anions were rapidly removed, supporting the very rapid formation of superoxide ion and so its direct involvement in these photoinduced oxygenations.

To further account for this latter statement, some years later, the same group reported that the DCA-sensitized photooxygenation of TS, nearly inert vs singlet oxygen, was highly modified upon the addition of benzoquinone (BQ) to the reaction mixture, attributing the change in the reaction course to the efficient interception of superoxide ion by BQ (exothermic by 0.47 V) [126].

In fact, the addition of BQ (10^{-3} *M*) to the reaction mixture reduced the rate of formation of benzaldehyde and minor products such as *trans*-stilbene epoxide and benzil, whereas no effect on the yield of *cis*-stilbene was observed (Scheme 4).

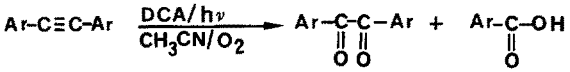


Scheme 4

This result, of course, substantiates the critical importance of superoxide ion in this DCA-sensitized reaction, owing to the contemporary inefficient reactions of the radical cation (TS^{+}) with molecular oxygen (Barton-type oxygenation), and also of the substrate, in the reported reaction conditions, towards singlet oxygen [85, 124]. In this regard, Foote and co-workers have recently reported a study on the singlet oxygenation of *trans*-stilbene and derivatives affording mono- and/or diendoperoxides along with variable amounts of the corresponding carbonyl compounds and oxiranes [127].

However, as we will see later on, other modes of evolution of the primary intermediate radical ions can be suggested to explain some oxidation reactions mediated by electron-transfer processes. In fact, several exceptions to the Foote's BQ-controlled photooxygenation procedure have been reported during the last years on several electron-rich substrates. Thus, the involvement of superoxide ion, as an oxygen active species, in all of the DCA-sensitized photooxygenations, remains questionable [96, 105, 112, 115, 128]. Schaap and co-workers [98] recorded under inert atmosphere the characteristic ESR spectrum of the $(\mathrm{DCA}^{\cdot-})$ radical anion. On the other hand, the involvement of aryl-olefin radical cations and their reactions with superoxide ion was easily observed by quenching experiments with compounds exhibiting lower oxidation potentials than those of aryl-olefins [85, 95, 98].

In fact, the addition of 1,4-dimethoxybenzene (DMB) and/or several similar compounds, at concentrations as low as 10^{-4} *M*, to a mixture of aryl-olefins and DCA almost completely inhibits the reactions. Concentration dependence and flash photolysis studies confirm that the primary electron-transfer process occurs between the singlet excited sensitizer and DMB ($E^{ox} = 1.34$ V vs SCE) with the generation of the corresponding radical ion pair. As a consequence, quantum yields lower than 1, even at infinite substrate concentration, are measured [95]. In this regard, valuable confirmations came from the cyanoaromatic photoinduced electron-transfer oxygenation of alkynes [99]. Farid and Mattes reported that the photooxygenation of diphenylacetylene DPA ($E^{ox} = 1.85$ V vs SCE) 25, leading to a mixture of benzil 26 and benzoic acid 27, was efficiently sensitized by DCA ($\Phi = 0.15$), but poorly by TCA ($\Phi < 0.001$) [Eq. (12)] [99].

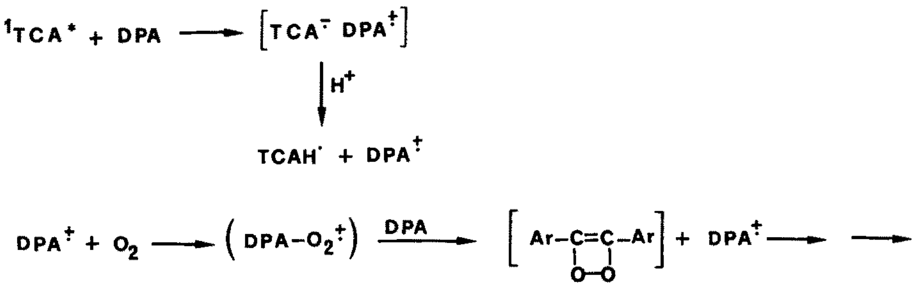


$$\mathrm{Ar{-}C{\equiv}C{-}Ar} \xrightarrow[\mathrm{CH_3CN/O_2}]{\mathrm{DCA}/h\nu} \mathrm{Ar{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}Ar} + \mathrm{Ar{-}\underset{\underset{O}{\|}}{C}{-}OH} \qquad (12)$$

This latter low quantum yield indicates that virtually none of the radical cation $(\mathrm{DPA}^{\cdot+})$ escapes out of the cage of the geminate pair $\mathrm{TCA}^{\cdot-}/\mathrm{DPA}^{\cdot+}$, owing to an exceptionally efficient reverse electron-transfer (which is unlikely), or that the reaction of $(\mathrm{DPA}^{\cdot+})$ with molecular oxygen is too slow to compete with the diffusion-controlled recombination of $(\mathrm{TCA}^{\cdot-})$ and $(\mathrm{DPA}^{\cdot+})$.

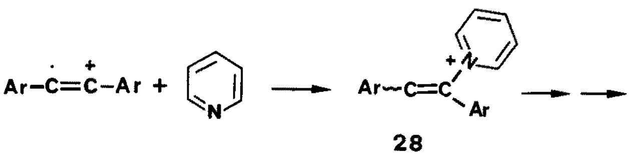
More interestingly, in the same report the authors observed that the quantum yield for the TCA-sensitized photooxygenation of 25 substantially increased by carrying out the reactions in the presence of catalytic amounts of acid (trifluoroacetic acid 10^{-2}–10^{-3} *M*) or nucleophiles such as pyridine, 2-*t*-butylpyridine, 4-picoline [99].

These chemical devices can be best explained in terms of protonation of the radical anion $(\mathrm{TCA}^{\cdot-})$ shown in Scheme 5. Or in terms of nucleophilic addition



Scheme 5

of pyridine to (DPA^{+}) with formation of a new radical cation intermediate 28 which is more reactive than (DPA^{+}) vs molecular oxygen:

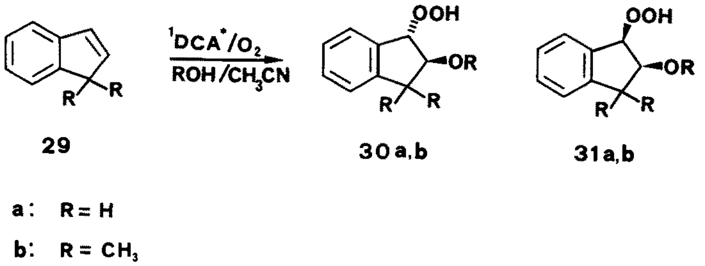


(13)

The interception of the radical anion by acid or the formation of 28 should have the same effect. In fact, the back electron-transfer reaction from (TCA^{-}) to (DPA^{+}) is suppressed, or at least reduced, maximizing the cage escape efficiency of the radical cation and its further reaction with molecular oxygen. In these reactions benzil 26 is probably formed via the dioxete intermediate, also suggested by de Mayo and co-workers [100], whereas the mechanism leading to benzoic acid is still uncertain. Other examples of photoinduced oxygenations, preceded by nucleophilic addition, have been also reported.

For dimethylindene (E^{ox} = 1.68 V vs SCE) 29, whose radical cation (29^{+}) is unreactive vs molecular oxygen, the DCA-sensitized photooxygenation proceeds well in the presence of a nucleophile (water or methanol) leading to a mixture of *trans*- and *cis*-hydroxy or methoxy-hydroperoxides 30a, b 31a, b:

The mechanism for the formation of these products involves nucleophilic addition of ROH to (29^{+}) with loss of a proton to form a benzylic free radical



(14)

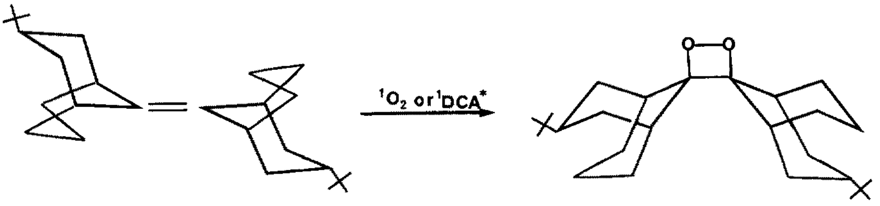
which then reacts with molecular oxygen. The peroxy radical is then reduced, probably by the sensitizer radical anion, and protonated to give the observed products [129].

Meanwhile, the methylene-blue-sensitized photooxygenation of 29 in CH_3OH/CH_3CN, besides a cyclic acetal, yields, sterospecifically, the *trans*-methoxy hydroperoxide derivative with regiochemistry opposite to that of 31b [129].

The difference in regiochemistry between the singlet oxygen and electron-transfer-sensitized photooxygenation of 29 probably arises from a different sequential addition of nucleophile and oxygen reactive species, as a result of different reactivities of the intermediates. Interception of intermediate radical cations by external and/or internal nucleophiles in photosensitized reactions have also been reported by Arnold [130], Foote et al. [131]. Thus, a different stereo- and/or regiochemical course of sensitized photooxygenation reactions should be desirable to place in order a diagnostic test for distinguishing between singlet oxygen and electron-transfer (both Foote-type and Barton-type) oxygenations.

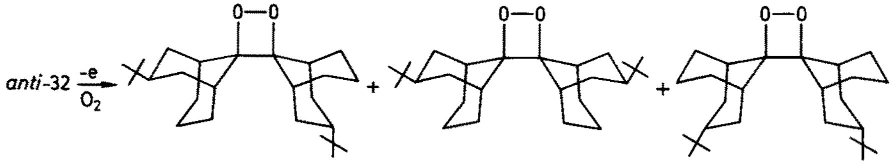
In this regard, Ando and co-workers [97, 116, 117] reported that sterically hindered olefins, affording remarkably stable dioxetanes [31, 132, 133], may be reliable molecules in the study of alkene reaction mechanisms.

As reported above, the singlet oxygen and/or DCA-sensitized photooxygenation of adamantylidene adamantane 21, a sterically hindered olefin, Bredt's rule protected, affords the corresponding stable dioxetane 23 through a plausible [2 + 2]-cycloaddition reaction between 21 and $^1O_2$, or by reaction of the corresponding radical cation ($21^{\dot{+}}$) with superoxide ion [34, 98]. However, in the latter case, the fact that electron-transfer quenching reaction between the two species can generate singlet oxygen makes this reaction dificult to quantify [113]. Moreover, 21 undergoes an easy electrode-catalyzed [121] and/or thermally induced oxygenation [120] through a chain radical cation electron-transfer process, in which the active oxygen species is the triplet molecular oxygen. As a consequence, with substrates whose radical cations are oxygen sensitive, it is not clear when the [2 + 2]-cycloaddition reaction goes by way of singlet oxygen, and/or electron-transfer (Foote-type) or Barton-type processes.



(15)

On the contrary, a different stereochemical course was observed in the dye-singlet, DCA-photosensitized and electrode-catalyzed oxygenations of two stereoisomeric derivatives such as *syn*- and *anti*-di-*tert*-butylbis(bicyclo [3.3.1] non-9-ylidenes) 32. In fact, the tetraphenylporphine (TPP) and/or DCA-sensitized photooxygenation of *anti*-32 gave a single dioxetane, *cis,trans*-33, Eq. (15), whereas the electrode-catalyzed oxygenations of both the isomers, *syn*- and/or *trans*-32 led to a mixture of all three possible dioxetanes, i.e., *cis,cis*-33, *cis,trans*-33, and *trans,trans*-33. In particular, *anti*-32, afforded the following reaction mixture [117]:



cis,trans-33 (34%) *cis,cis*-33 (24%) *trans,trans*-33 (24%)

(16)

In the light of these results, photooxygenations of *syn*-32 by either TPP or DCA-sensitized reactions afforded, as expected, a mixture of two dioxetanes *cis,cis*-33 and *trans,trans*-33. Clearly, the dye-sensitized photooxygenations of *anti*- and/or *syn*-32 are stereospecific in the fashion described for the concerted cycloaddition of singlet oxygen [32]. Instead, the electrode-catalyzed oxygenations are not stereospecific and this behavior is consistent with the Barton-type mechanism [125]. In other words, the intermediate radical cations undergo an extensive isomerization prior to reacting with molecular oxygen. Surprisingly, the DCA-sensitized reaction, presumably proceeding by way of radical cation-superoxide ion reaction, also occurs stereospecifically and, of great interest, in contrast to that previously reported by Foote [95], the recovered olefin retains its configuration. Different hypotheses can be advanced: (i) the reaction between the radical cation and superoxide ion is fast enough to avoid any isomerization of the intermediate radical cation; (ii) the DCA-sensitized reaction produces, as suggested by Foote and Santamaria [113, 119], singlet oxygen in the reaction medium. In conclusion the stereochemical oxidation of the hindered olefin 32 can act as a useful tool for distinction between the Barton-type and the singlet or Foote-type oxygenations. As a consequence of Ando's preliminary results, the interest of the same and several other groups was centered on the reactivity of a wide variety of hindered olefins whose corresponding radical cations can be oxygen sensitive or not.

Nelsen and co-workers [134] extended these studies to olefins having methyl substitution, such as isopropylidene-adamantane 34, demonstrating that the protection of all alkyl groups is not necessary, in certain conditions, for efficient dioxetane formation. In fact, the singlet oxygen and/or DCA-sensitized photooxygenations of 34, leading to the corresponding ene product, fail to make the dioxetane 35, which is meanwhile easily prepared by reaction of the same substrate with catalytic amounts of one electron-oxidizing reagents such as tris-(*o,p*)-

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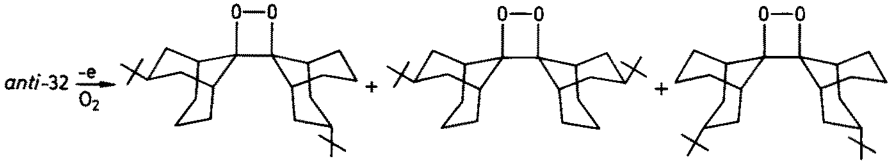

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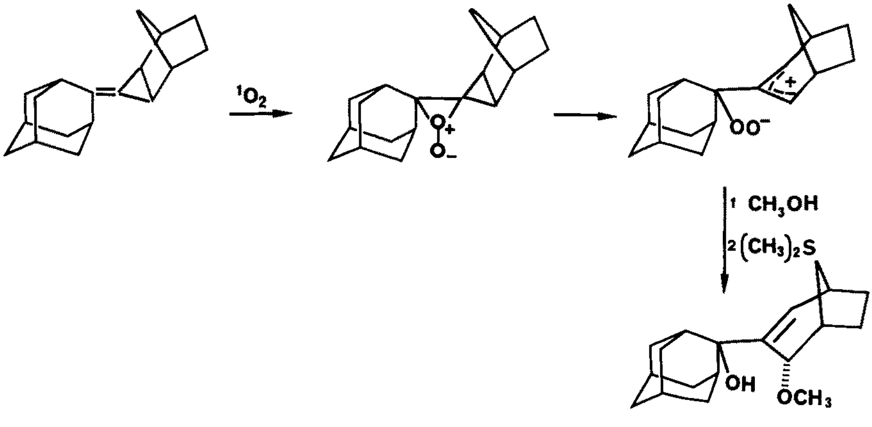
to give a perepoxide or a zwitterionic peroxide intermediate followed by cyclization to *endo*-38. In this regard, the interception of the peroxide species by alcohol with formation of the adduct 39 constitutes a clear evidence for a zwitterionic intermediate (Scheme 6).



39

Scheme 6

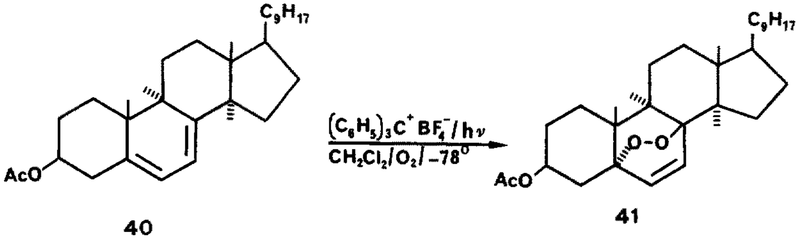
The DCA-sensitized reaction on 37, showing a different stereochemical course and requiring the presence of *trans*-silbene as a cosensitizer, renewed the interest in the indirect DCA-sensitized photo-stilbeneoxygenations of organic substrates, formerly described by Foote, Schaap, and co-workers [50, 94, 135]. Since TS is present in high concentrations, the photooxygenation of 37 proceeds via initial formation of the radical cation ($TS^{+\cdot}$), followed by exoergonic electron-transfer from 37 to ($TS^{+\cdot}$) to give ($37^{+\cdot}$). The subsequent reaction between the substrate radical cation and superoxide ion may occur stereospecifically at less hindered *exo* face of the molecule to give the zwitterionic peroxide and subsequent cyclization to *exo*-38.

Furthermore, the radical cation ($37^{+\cdot}$), produced by electrolysis and/or by the use of one-electron-oxidizing agents, appears totally inert vs triplet molecular oxygen, envisaging, also in this case, an inefficient Barton-type reaction. The whole of these complex results, of course, induce an easy question: what factors control whether radical cations, chemically and/or photochemically generated, react with oxygen species or not?

The authors, on the basis of their experimental results, pointed out that olefin radical cations-allylically methylated and/or stabilized by heteroatoms or π conjugation [136] do not react with an active oxygen species, suggesting, in spite of their low oxidation potentials, that several factors may contribute to determine this behavior. Thus, one of the important factors is the presence of an independent π-system in which odd-electron density is not delocalized, whereas, a second and a third factor can be the insufficient steric hindrance to block the attack of oxygen on the olefin radical cation face and an oxidation potential of the substrate higher than 1.7 V vs SCE.

Of course, the combined efforts of several groups will be of great importance in order to define the actual mechanisms operating in the photo and/or thermally-induced oxygenation of these olefins. Finally, it is claimed that substrate 37 can be used as a mechanistic probe to substantiate that the dye (RB) and/or (MB^+)-sensitized photooxygenations may involve concomitantly a singlet oxygen and an electron-transfer process. In fact, on the contrary to other cases [73, 137], these reactions afford a mixture of *endo*- and *exo*-38 arising from the two different mechanistic pathways, i.e., singlet oxygenation, and a chain electron-transfer process.

In the early 70s, Barton and co-workers reported that irradiation of a mixture of ergosteryl acetate 40 and a new non conventional electron acceptor, i.e., trityltetrafluoroborate $(C_6H_5)_3C^+BF_4^-$, in methylene chloride in the presence of oxygen at −78° led quantitatively to the corresponding 5α,8α-ergosteryl peroxide 41 [125]:

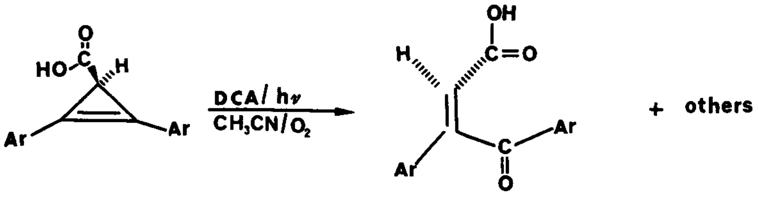


(20)

Further investigation showed that non-transition-metal Lewis acids ($SnCl_4$, SbF_5, BF_3, etc.) can act as effective catalysts for the photooxygenation in Eq. (20), whereas triarylaminium radical cations, bearing one or more electronegative para substituents, and transition-metal-Lewis acids ($FeCl_3$, $FeBr_3$, WCl_6, $MoCl_5$, $VOCl_3$) induced the oxygen of several dienes without irradiation [138, 139].

For the oxygenation of 40 to 41, in the dark and in the presence of catalytic amounts of tris(*p*-bromophenyl)ammoniumyl tetrafluoroborate, $(p\text{-}BrC_6H_4)_3N^{+\cdot}BF_4^-$, Tang and co-workers [140] proposed a chin electron-transfer pathway, suggesting at the same time that the same mechanism could operate in the trityl cation and Lewis acid-catalyzed oxygenations.

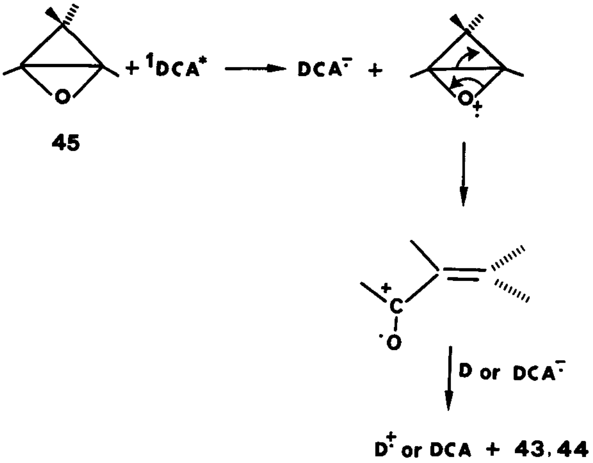
As a consequence, the interest of many groups was centered around possible reactions of radical cations with molecular oxygen even in the DCA-sensitized reactions. In this regard, contemporary to Foote's reports dealing with the DCA-sensitized photooxygenations of alkenes, dienes, and sulfides [84], Farid and co-workers reported that the DCA-sensitized photooxygenation of 1,2-diphenylcyclopropene-3-methylcarboxylate (DCMC) 42 led to a mixture of *cis*- and *trans*-3-benzoyl-3-phenylmethylpropenoate 43, 44 together with benzil, benzoic acid, benzoic anhydride, and several unidentified minor products [106, 141]:



42 **43, 44** (21)

On the basis of a quantum yield as great as 20, they suggested a chain radical cation electron-transfer oxidation, initiated by the reaction of the radical cation (DCMC$^{+\cdot}$) with O_2 with formation of the oxygenated radical cation (DCMC-$O_2^{+\cdot}$).

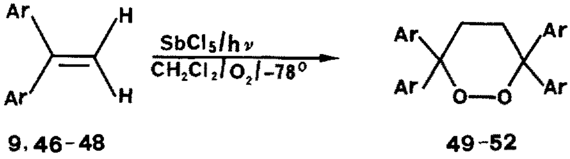
However, we believe that the primary intermediate might be the corresponding oxabicyclo derivative, 45, which can undergo a chain electron-transfer isomerization into the corresponding carbonyl compounds 43, 44 (Scheme 7).



Scheme 7

Recent results on the isomerization of epoxides to ketones accomplished via electrode-catalyzed, one electron-oxidizing reagents, and DCA-sensitized photoreaction under nitrogen atmosphere, seem to confirm this mechanistic pathway [142, 143]. On the other hand, the MCPBA oxidation of 42 affords the same reaction products 43, 44, through a plausible acid-catalyzed isomerization of the same intermediate 45 [144].

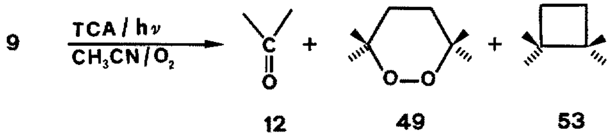
Haynes [145] found that 1,1-diarylethylenes (DAE) 9, 46–48 are converted, in high yields (80–90%), into the corresponding 3,3,6,6-tetraaryl-1,2-dioxanes 49–52 by irradiation with a tungsten lamp at −78° of their oxygenated methylene chloride solutions in the presence of antimony(V) chloride:



(22)

9: Ar = C_6H_5; 46: Ar = p-$CH_3C_6H_4$; 47: Ar = p-$CH_3OC_6H_4$; 48: Ar = p-t-$C_4H_9C_6H_4$

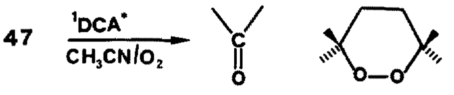
It was suggested that the olefin radical cations, formed upon irradiation of the CT complex of the olefins with $SbCl_5$, react with the corresponding neutral olefins to give dimeric radical cations, whose reactions with molecular oxygen and subsequent reductions would lead to the dioxanes. Similar results wee also obtained in the TCA-sensitized photooxygenation of 9 [71]:



(23)

To account for the results described in Eq. (23), two unconnected and simultaneous mechanisms can be suggested, i.e., a chain electron-transfer mechanism, leading to 1,2-dioxane together with 1,1,2,2-tetraphenylcyclobutane 53, and the classical Foote mechanism, affording the carbonyl compound.

Some years later, Gollnick and Schnatterer [96] reported, on the contrary to Foote's data [84], that also the DCA-sensitized photooxygenation of several similar 1,1-diaryl-substituted olefins (E^{ox} lower than 2 V vs SCE) yielded the corresponding 1,2-dioxanes (90%) together with the corresponding carbonyl compounds:

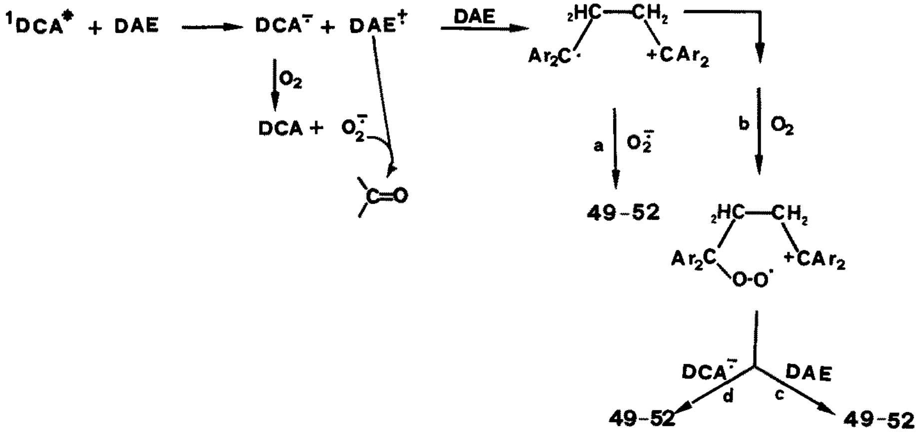


(24)

To account for these original results, the authors pointed out that the purity of the acetonitrile, the reaction solvent, was of critical importance. In fact, with a solvent crop not freshly purified, a decreased oxygen uptake rate, along with decreased amounts of 1,2-dioxanes, was observed.

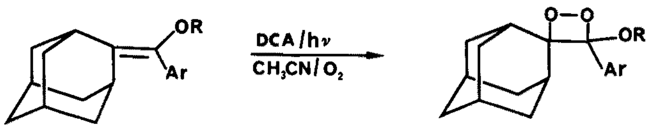
Since the 1,1-diarylethylenes quench efficiently the DCA-fluorescence, it is safe to assume that carbonyl compounds arise through Foote's mechanism.

On the other hand, in order to rationalize the formation of 1,2-dioxanes, the authors suggested the formation of dimeric radical cations by interaction of neutral olefins with the corresponding radical cations. Different pathways for the production of 1,2-dioxanes from dimeric radical cations can be envisaged: (a) direct interaction with superoxide ion; (b) interaction with molecular oxygen and subsequent formation of oxygenated dimeric radical cations, which can in turn transfer an electron with reduced sensitizer radical ion (path d), or with another molecule of 1,1-diarylethylene with formation of 1,2-dioxanes and the donor radical cations (path c) (Scheme 8).



Scheme 8

All pathways account for the fact that two molecules of substrate are consumed per one molecule of oxygen, however, the high limiting quantum yield for the disappearance of the olefin ($\Phi = 10$) strongly supports a chain electron-transfer mechanism (path c). On the same topic, it has been recently suggested that the DCA-sensitized photooxygenation of several alkoxy (aryl)-methylidene adamantanes 54–58 yield the corresponding thermally stable 4-alkoxy-(1-aryl) spiro[1,2-dioxetane-3,2'-adamantanes] 59–63 through a chain electron-transfer mechanism [128]:



54-58

59-63

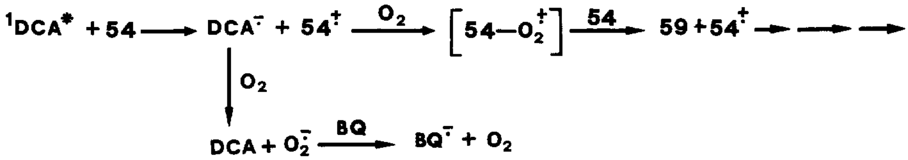
(25)

54: Ar = C_6H_5, R = CH_3; 55: Ar = 1-$C_{10}H_7$, R = CH_3; 56: Ar = 2-$C_{10}H_7$,R = CH_3; 57: Ar = C_6H_5, R = $C_6H_5CH_2$; 58: Ar = $C_{12}H_{10}$, R = CH_3

The key step in these DCA-sensitized photooxygenations of enol ethers, involves a diffusion-controlled rate electron-transfer fluorescence quenching of the singlet excited sensitizer by the donors (E^{ox} in the range 1.24–1.30 V vs SCE) with the generation of the radical ion pairs. Seemingly, formation of the ultimate products 59–63 could be easily rationalized on the basis of the classical Foote mechanism

[84]. However, the proneness of these substrates to undergo an easy singlet oxygen functionalization [31], as well as an exceedingly fast oxygenation of the corresponding ($54-58^{+}$) radical cations, thermally generated by reaction with catalytic amounts of one-electron-oxidizing agents, *namely* tris(*p*-bromophenyl) ammoniumyl hexachloroantimonate [146–149], induced the authors to deeply investigate the actual mechanism operating in these DCA-sensitized reactions.

The very high limiting quantum yield calculated for the DCA-sensitized photooxygenation of 54 (Φ = 23.8) [115], together with the cyclic voltammetric spectra (Fig. 2a, b) recorded under inert and/or oxygen atmosphere [146], strongly support the following chain electron-transfer mechanism (Scheme 9).



$$\begin{tikzcd} {}^1DCA^* + 54 \arrow[r] & DCA^{\cdot -} + 54^{\cdot +} \arrow[r, "O_2"] \arrow[d, "O_2"] & \left[54-O_2^{\cdot +}\right] \arrow[r, "54"] & 59 + 54^{\cdot +} \arrow[r] & {} \arrow[r] & {} \arrow[r] & {} \\ & DCA + O_2^{\cdot -} \arrow[r, "BQ"] & BQ^{\cdot -} + O_2 \end{tikzcd}$$

Scheme 9

Moreover, of great interest from the mechanistic point of view, appear the quenching experiments carried out in the presence of benzoquinone BQ, and 1,4-diazabicyclo[2.2.2]octane DABCO. In fact, the absence of any appreciable effect on the DCA-sensitized photooxygenation rate of 54 in the presence of BQ, an efficient superoxide quencher [150], leaves out the exclusive involvement of

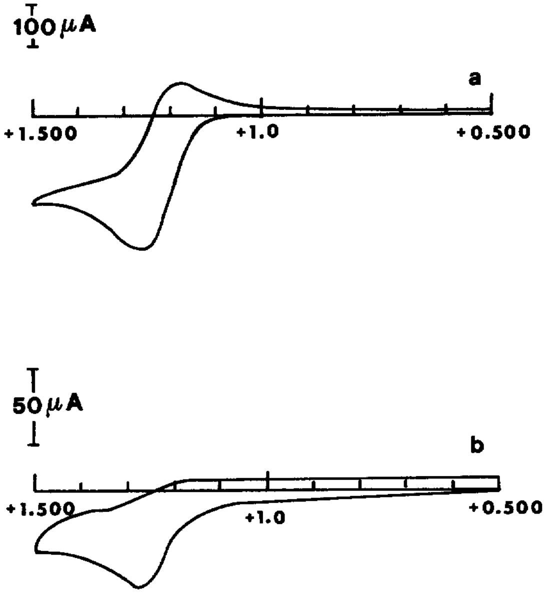
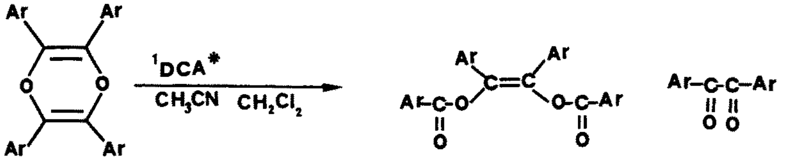


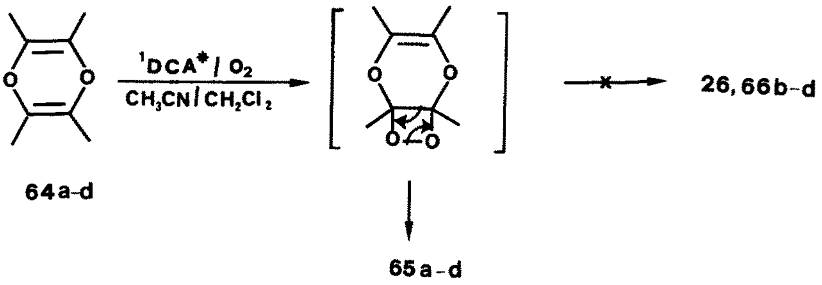
Fig. 2a, b. Cyclic voltammogramms of 54 in argon saturated (**a**) and oxygen saturated solutions (**b**).

superoxide ions as oxygen active species (Scheme 9). On the other hand, the inhibition, which goes from total to partial, observed in three different reactions carried out on 54, in the presence of progressively reduced amounts of the efficient singlet oxygen quencher DABCO [151] can be due mainly to an easier electron-transfer reaction between $^1DCA^*$ and DABCO ($E^{ox} = 0.64$ V vs SCE [152], rather than to its action as singlet oxygen quencher. Thus, the formation of enol ether radical cations, and their subsequent chain electron-transfer reaction will be reduced, depending on DABCO concentration. Similar conclusions, also reported by Mizuno et al. [104], had been advanced in the DCA-sensitized photooxygenation of substituted-2,3,5,6-tetraphenyl-*p*-dioxins 64a–d leading to a mixture of (*Z*)-stilbendioldibenzoates 65a–d and the corresponding α-diketones 26, 66b–d [112, 153]:



64a–d 65a–d 26,66b-d (26)

$64a: Ar = C_6H_5; 64b: Ar = p\text{-}CH_3OC_6H_4; 64c: Ar = p\text{-}CH_3C_6H_4; 64d: Ar = p\text{-}ClC_6H_4$



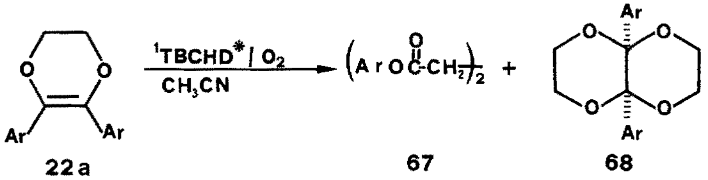
Scheme 10

Differently from previous data [154] which claim the formation of two equivalents of benzil through an unusual cleavage of the intermediate monodioxetane, in this report it is pointed out that 65a–d arise from the normal fragmentation of the thermally unstable intermediate with total breaking of the dioxetanyl carbon – carbon bond, whereas an unconnected mechanism would afford the α-diketones (Scheme 10).

Furthermore, the modest effect exhibit by BQ and by DABCO can be explained as previously reported.

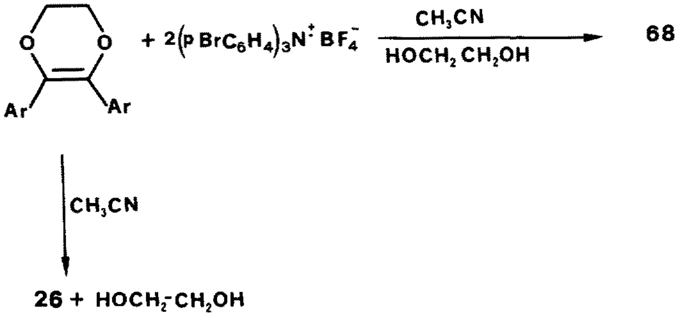
Actually, the substrates being reactive vs singlet oxygen, whose formation in the DCA-sensitized photooxidations has been already observed by Foote [119] and Santamaria [113], the author suggests a singlet oxygenation process on 64a–d that would account for 65a–d, whereas a disproportionation process of the intermediate radical cations, as we will see later on, would be responsible for the syntheses of α-diketones 26, 66b–d. The Rose bengal-sensitized photooxygenation of the same substrates, affording a mixture of bisdioxetanes, monodioxetanes, and variable amounts of the corresponding α-diketones, strongly supports that the RB-sensitized photooxygenations may involve both singlet oxygen and an electron-transfer process, which produces donor radical cations undergoing different processes, including disproportionation, in relation to the reaction conditions [75, 117, 155, 156].

In this regard, clear chemical and spectroscopic evidence for the disproportionation of the intermediate radical cations, photochemically and/or thermally generated, were achieved on 2,3-diphenyl-5,6-dihydro-1,4-dioxin, and derivatives 22a–c [90, 111, 57–159]. In fact, the 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one (TBCHD)-sensitized photooxygenation of 22a affords the corresponding 1,2-ethanedioldibenzoate, 67, the cleavage product of the intermediate 1,2-dioxetane, 24a, together with minor amounts of 4a,8a-diphenyl-2,3,4a,6,7,8a-hexahydro-*p*-dioxino[2,3-b]-*p*-dioxin 68 [158]:



(27)

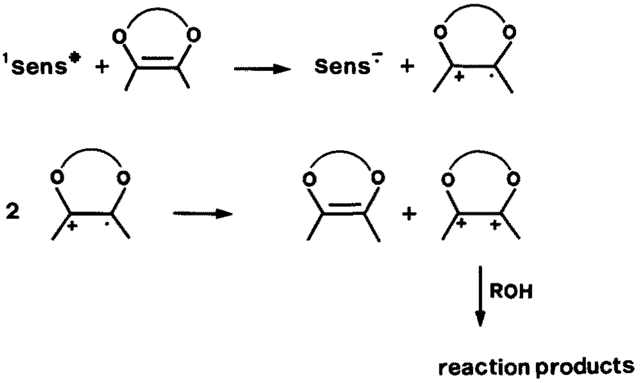
The latter *cis*-1,6-diphenyl-tetraoxobicyclo[4.4.0]-decane, 68, becomes the only reaction product when 22a, in acetonitrile ethylene glycol mixtures, is treated with two equivalents of tris-(*p*-bromophenyl)ammoniumyl tetrafluoroborate, a one-electron oxidizing agent. The same reaction, carried out in methylene chloride and/or acetonitrile, yields benzil together with the corresponding glycol [159]:



(28)
(29)

Experimental proofs suggest that α-diketones could arise from a mechanism still involving dioxene radical cations as intermediates. Schaap and co-workers

[98], discussing the DCA-sensitized photooxygenation of dioxenes 22a–c, advanced the hypothesis that a chain mechanism involving disproportionation of dioxene radical cations, and their subsequent reaction with superoxide ion, was conceivable on the basis of thermodynamic considerations (Scheme 11).



Scheme 11

In fact, the disproportionation of dioxene radical cations can be substantiated by cyclic voltammetric studies, since they show a second irreversible oxidation wave, with a peak potential 0.2–0.5 V more positive than the half-wave potentials. In addition to the chemical proofs [see Eqs. (28, 29)], further evidence supporting the disproportionation of dioxene radical cations were achieved by NMR and

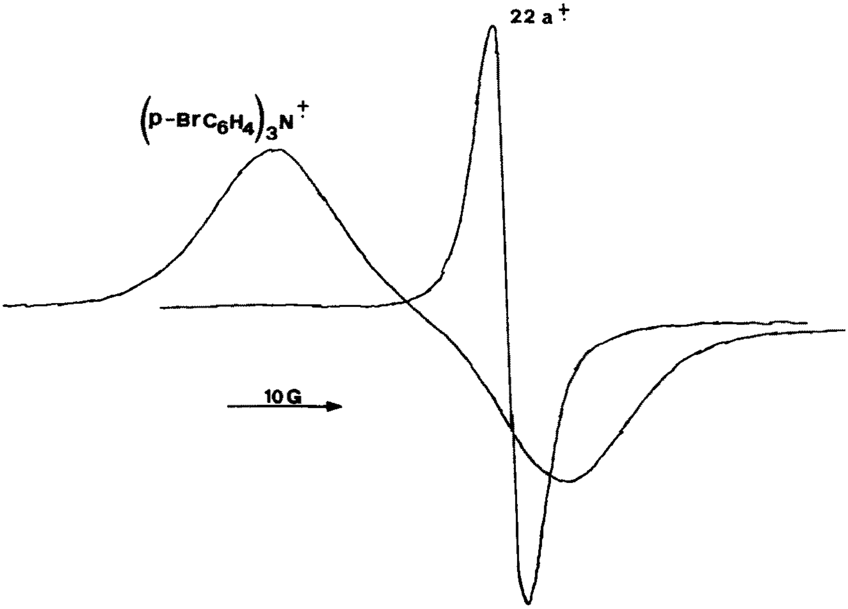


Fig. 3.

ESR spectroscopies. In fact, the addition of one equivalent of 22a–c to an acetonitrile solution of aminium salt causes the replacement of the ESR signal of the aminium radical cation with a broad singlet signal shifted at a higher field (Fig. 3).

These new resonances due to the radical cations ($22a-c^{+}$) decrease with the fading of the dark-red solutions, and the decay appears to be second order in substrates. In conclusion, the stoichiometric requirement of two equivalents of the one-electron oxidizing agent yielding benzil derivatives, the valuable spectroscopic data, the easy interception of the doubly charged ions by nucleophiles, straightforwardly support the hypothesis that peculiar radical cations may disproportionate to give a doubly charged ion and neutral substrates, and that the interception of dications by nucleophiles seems apparently faster than the chain oxidation reaction, as suggested by Schaap, see Scheme 11 [75, 98, 111, 112, 159].

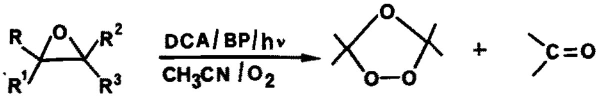
Further support to this mechanism came from the concomitant ESR, CV, and chemical studies on the evolution of the radical cation ($64a^{+}$), generated in the same way, and leading essentially to benzil 26 [111, 112].

The doubly charged ion can also be easily trapped by nucleophiles [75, 156–159]. The whole of the experimental results described in this section open a puzzle question about the actual mechanism operating in the sensitized photooxygenation of donors with different chemical features.

In fact, as described above, Foote et al. [127] reported that the DCA-sensitized photooxygenation of *trans*-stilbene, nearly inert vs singlet oxygen, was modified upon the addition of BQ, and they attributed the change in the reaction course to an efficient interception of superoxide ion by BQ. On the contrary, as reported above, the involvement of superoxide ion is oxygen active species in all the DCA-sensitized reactions appears questionable. In fact, it seems reasonable to suggest that the efficiency of BQ inhibition is strictly related to the peculiar features of the donors. This procedure, stressed in the next section, could, of course, constitute a mechanistic probe to discriminate among the three different mechanistic pathways leading to the oxygenated derivatives.

4 Cosensitized Cyanoaromatic-Sensized Photooxygenation of Organic Substrates

Some years ago, Schaap and co-workers developed a method by which compounds that do not quench the fluorescence of the singlet excited DCA sensitizer may nevertheless be rapidly oxidized [102, 108, 109, 160–162]. For example, epoxides 69a–d, unreactive under standard DCA-sensitized conditions [107, 163], can be readily converted into the corresponding ozonides 70a–c, in high yields, by use of a non-light-absorbing aromatic hydrocarbon, i.e., biphenyl (BP) as a cosensitizer in conjunction with DCA. Variable amounts of carbonyl compounds, such as benzophenone from 69a, b, benzaldehyde from 69b, c, d are also formed [162]:

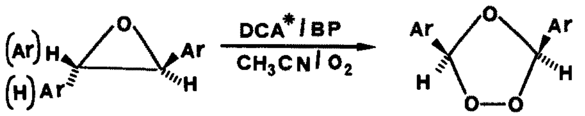


69a-d 70a-c

(30)

69a: $R = R^1 = R^2 = R^3 = C_6H_5$; 69b: $R = R^1 = R^2 = C_6H_5$, $R^3 = H$;
69c: $R = R^2 = H$, $R^1 = R^3 = C_6H_5$; 69d: $R = R^3 = H$, $R^1 = R^2 = C_6H_5$

In all cases the corresponding ozonides, 70a–c, have been shown to be stable under the reaction conditions, whereas preliminary experiments suggested that small amounts of water in the reaction medium can result in the formation of carbonyl products, possibly through interception of the intermediate radical cations [164]. An alternative explanation, accounting for the formation of carbonyl compounds, might involve cleavage of the intermediate carbonyl ylides, as actually suggested in Griffin's work on the photoelimination of aryloxiranes [165]. HPLC analysis indicated that BP was not appreciably consumed during these photooxygenations, and that the epoxides were not oxidized upon irradiation for long time with a 400-W high-pressure sodium lamp in oxygenated-acetonitrile solutions containing RB as triplet exicited sensitizer. More interestingly, the DCA/BP cosensitized photooxygenations of *cis*- and/or *trans*-69c, d, as well as the DCA-sensitized photo-reactions on several *cis*- and *trans*-2,3-dinaphthyloxiranes 69e–h, with oxidation potentials in the range of $E^{ox} = 1.50–1.59$ V. vs SCE, and consequently, not requiring the BP cosensitization, afforded exclusively the corresponding *cis*-ozonides 70a–e:



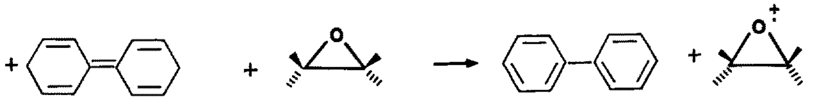
69 70

(31)

69e: $R^1 = R^3 = H$, $R = R^2 = 1\text{-}C_{10}H_7$; 69f: $R^1 = R^3 = H$, $R = R^2 = 2\text{-}C_{10}H_7$; 69g: $r = R^3 = H$, $R^1 = R^2 = 1\text{-}C_{10}H_7$; 69h: $R = R^3 = H$, $R^1 = R^2 = 2\text{-}C_{10}H_7$

In the latter case [166], the stereochemistry of the *cis*-3,5-bis(2′-naphthyl)-1,2,4-trioxolane 70e has been unequivocably assigned by X-ray structure and by chromatographic resolution using HPLC chromatography, with optically active (+)-poly(triphenylmethyl methacrylate) as the stationary phase.

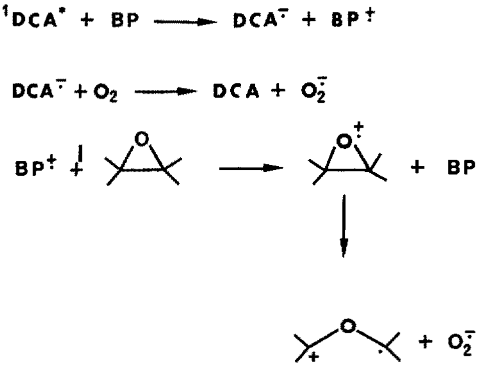
Although the mechanism of the DCA/BP-cosensitized photooxygenation of epoxides to ozonides has not yet been fully delineated, a plausible mechanism, consistent with the available results, involves a preliminary fluorescence quenching of singlet excited DCA by BP ($E^{ox} = 1.84$ V vs SCE), much easier to oxidize, with the exception of 69e–h, than all the other epoxides 69a–d ($E^{ox} > 2$ V vs SCE), with the concomitant formation of the primary radical ion pair ($DCA^{-\cdot}BP^{+\cdot}$), eventually leading to free radical ions. These latter radical ions may undergo secondary electron-transfer reactions, and, limitately to electron-donors, the primary radical cation $BP^{+\cdot}$ can be replaced by secondary ones. The reactions will occur at a diffusion-controlled rate when the oxidation potential of the cosensitizer, the primary donor, is sufficiently higher than those of the secondary donors:



(32)

The secondary electron-transfer processes, often used in mechanistic investigations and in preparative applications of electron-transfer photochemistry, enhance the quantum yields of product formation [167]. In fact, as we have already pointed out in a previous section, the efficiency of separation of the geminate pair is strictly dependent on the redox potentials (see also indirect photooxygenation processes) [43, 50, 80–83, 135]. Anyway, although in the present case the subsequent electron-transfer from epoxide to biphenyl radical cation $BP^{+\cdot}$ is endothermic enough, in the absence of very fast competing reactions this primary radical cation may still undergo an endothermic electron-transfer process with epoxides.

Actually, this seems the key step in Schaap's procedure [160, 162]. In fact, although energetically unfavorable, a reversible electron-transfer reaction from



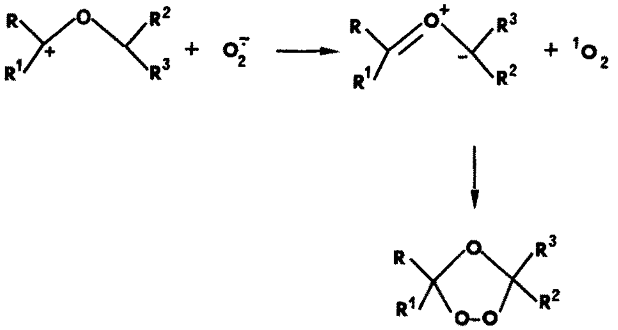
Scheme 12

epoxides to $BP^{+\cdot}$ would generate the corresponding unopened epoxide radical cations. This step would be driven by the subsequent irreversible generation of the ring-opened radical cations and, eventually, subsequent trapping by superoxide ion would yield the ozonides (Scheme 12).

An important factor in the oxidation of epoxides by $BP^{+\cdot}$ to their corresponding radical cations would certainly be the much longer lifetime of $BP^{+\cdot}$ compared to that of singlet excited DCA-sensitizer. Farid et al. advanced a similar hypothesis in the dimerization of dimethylindene, initiated by reaction of 9-cyanoanthracene or fluorenone in the presence of aromatic hydrocarbons, with oxidation potentials lower than that of the substrate, as a cosensitizer [168]. Even in this case, because of the much longer living primary hydrocarbon radical cation, an endothermic electron-transfer process, favorably competing with the decay pathways, would populate the radical cation of dimethylidene. Pac et al. have also studied several reactions based on secondary electron-transfer processes [169, 170].

However, Schaap's results are not consistent with a mechanism involving attack of superoxide ion on the opened radical cations. In fact, the striking stereochemical course could be accommodated only by admitting the formation of the most stable E-E conformation of epoxide radical cations, and by showing that the ring closure of the zwitterion intermediates could occur faster than the bond rotation.

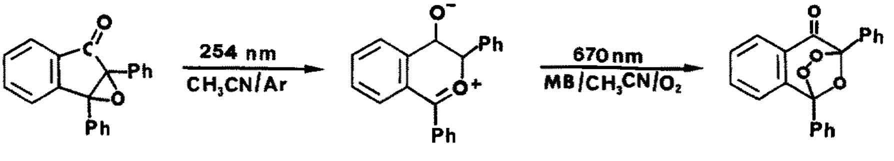
Thus, a more convincing mechanism would involve reduction of the *E-E* conformation of the radical cations by superoxide ion to yield the *E-E* conformation of the corresponding carbonyl ylides and singlet oxygen. The subsequent [4 + 2]-cycloaddition would afford the ozonides. Foote had shown that singlet oxygen can be formed in photosensitized oxygenations by energy-transfer from triplet excited ^{3}DCA* to oxygen [119, 203], wehereas Santamaria suggested singlet oxygen formation as a result of the back electron-transfer from superoxide ion to the radical cation [111] (Scheme 13).



Scheme 13

The proposed intermediacy of carbonyl ylides and their reactions with singlet oxygen are in accord with similar observations on trapping the photogenerated carbonyl ylides [164, 171–178].

For example, Griffin and Miyashi with their respective co-workers [176–178] have confirmed that ylides can be trapped by dipolarophiles affording substituted tetrahydrofurans with an identical stereochemical course. In a related work, Arnold [164] has utilized 1,4-dicyanonapthalene, an electron-transfer sensitizer, with epoxides in the presence of dipolarophiles to yield substituted tetrahydrofurans in which the major products have a *cis*-diphenyl relationship. Trozzolo has used spectroscopic methods to characterize carbonyl ylides produced by photochemical cleavage of epoxides [174]. Finally, Ulmann and Henderson [179] demonstrated that 2,3-diphenyl indenone oxide, 71, and the corresponding ylide, 72, were photochemically interconvertible, and, if the photolysis occurred in the presence of oxygen, a reaction product directly derived from the decomposition of the corresponding ozonide 73 was formed:

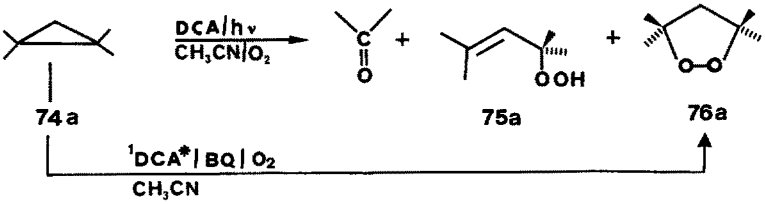


71 72 73

(33)

The re-examination of this reaction led Schaap's group to provide the first direct evidence for the formation of an ozonide from a singlet oxygenation of a photochemically generated carbonyl ylide. Additional insight into the mechanism of DCA/BP cosensitized photooxygenation of epoxides can also be obtained considering an analogous process, i.e., the homogeneous redox catalysis of electro-reduction of aliphatic halides (RX). In fact, electrochemically generated hydrocarbon radical anions act as catalysts. The electron transfer from these radical anions to RX form the unstable radical anion ($RX^{\bar{\cdot}}$) with the contemporary regeneration of the hydrocarbon species. Although this step is energetically unfavorable, it is driven by the irreversible cleavage of the radical anion ($RX^{\bar{\cdot}}$) into an alkyl radical and halide anion [180].

Cosensitization by BP may also provide rate enhancements for photooxygenations of substrates that are in fact better quenchers of $^1DCA^*$ than BP. As an example, 1,1,2,2-tetraphenylcyclopropane 74a (E^{ox} = 1.48 V vs SCE) quenchs $^1DCA^*$ more efficiently than BP. Notwithstanding this, the rate of photooxygenation of 74a can be increased by more than a factor of 10 by addition of an equimolecular amount of BP [103]. More interestingly, the reaction course is also modified by addition of BP. In fact, the DCA-sensitized photooxygenation of cycloalkanes, and for example of 74a, leads to a mixture of hydroperoxide 75a and benzophenone together with minor amounts of the corresponding 3,3,5,5-tetraphenyl-1,2-dioxolane 76a, a major reaction product in the BP-cosensitized reaction [103, 109]:



74a 75a 76a

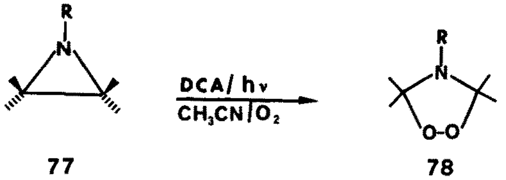
(34)
(35)

The stereochemical course is not striking as in the former case observing, on appropriate cycloalkanes, a mixture of isomeric 1,2-dioxolanes. The ratio does not change during the irradiation [109]. In this case, to account for the catalysis of BP, Schaap et al. suggested a higher cage escape efficiency of the radical cation ($BP^{+\cdot}$) from the radical ion pair, compared with that of the radical cation ($74a^{+}$). Thus, the secondary exothermic electron transfer between 74a and ($BP^{+\cdot}$) (exothermic by ca. 0.5 eV) is expected to occur at diffusion-controlled rate.

This explanation, as reported in a previous section, suggested by Farid [80] and Mataga [81], has been recently confirmed by Farid and Gould [83]. In other words, they claim that the rate constant k_b for the singlet recombination is thought to decrease as the exothermicity increases. These results have also been explained in terms of the gap theory for radiationless decay and the Marcus "inverted region" of electron transfer [66, 83].

The above considerations suggest that the most effective cosensitizers for DCA-sensitized reactions will be those with oxidation potentials in the range 1.8–2.0 V vs SCE. In fact, in this range the cosensitizers will poorly quench the $^1DCA^*$ fluorescence, but will have high enough oxidation potentials to maximize the cage escape efficiency of the radical cation from the pair in order to facilitate secondary electron-transfer processes with the substrates.

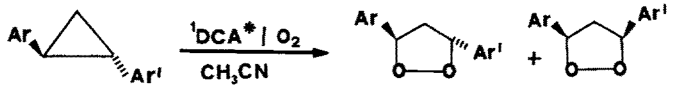
Finally, the DCA-sensitized photooxygenations of several substituted or unsubstituted aziridines, affording the corresponding 1,2,4-dioxazolidines, do not require the BP cosensitization since they efficiently quench the $^1DCA^*$ fluorescence [109, 181, 182]. Of particular interest is the fact that the unsubstituted derivatives *cis*- and/or *trans*-2,3-diphenylaziridines 77a, b follow a similar stereochemical course of epoxides with the exclusive formation of the *cis*-isomer 3,5-diphenyl-1,2,4-dioxazolidine 78:



(36)

This result, also explained in terms of a mechanism involving trapping of the more stable azomethine ylide intermediate by singlet oxygen, finds confirmation on the observation that in the photooxygenations of N-substituted isomeric aziridines, the *cis*- to *trans*-ratio of isomeric 1,2,4-dioxazolidines is inversely related to the size of the group on nitrogen.

Independently and concomitantly, similar conclusions on the electron-transfer photooxygenations of several substituted 1,2-diarylcyclopropanes, 79a–d, affording the corresponding 1,2-dioxolanes, 80a–d, in high yields as well as high quantum yield efficiency, were published by Mizuno's group [104]:



(37)

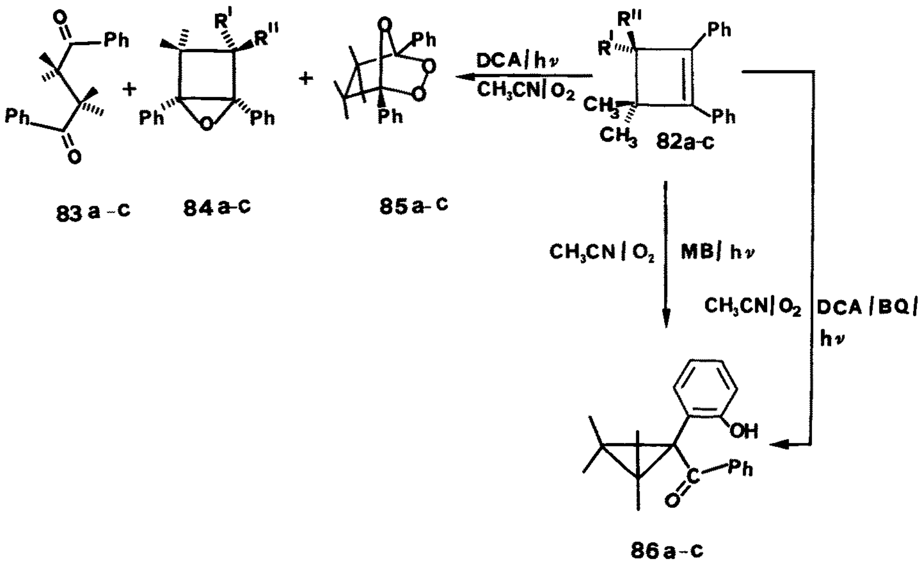
79a-d **80a-d**

79a: Ar = Ar' = 4-MeOC$_6$H$_4$; 79b: Ar = 4-MeoC$_6$H$_4$, Ar' = 4-MeC$_6$H$_4$; 79c: Ar = 4-Me$_2$NC$_6$H$_4$, Ar' = C$_6$H$_5$; 79d: Ar = Ar' = 3,4-(Meo)$_2$C$_6$H$_3$

In fact, these photoreactions, in spite of the oxidation potentials of the substrates, which are lower than 2 V, are greatly accelerated by the addition of certain aromatic hydrocarbons such as BP and phenanthrene, or by metal salts, such as LiBF$_4$ and Mg(ClO$_4$)$_2$, whereas they are completely quenched by the addition of triethylamine TEA and DABCO, and no photooxygenation takes place in nonpolar solvents. Contrarily to the observations of Schaap's group [103], the course of these reactions is not modified upon the addition of additives, yielding, at different times, a similar mixture of isomeric 1,2-dioxolanes (95–99%), along with traces of by-products directly arising from the subsequent electron-transfer oxidation on the major reaction products, i.e., 80a–d. These results strongly suggest that, in the DCA-sensitized reactions on 1,2-cycloalkanes, the radical ion pairs are produced spontaneously upon excitation of DCA specifically in polar solvents. As already reported, the critical factor determining the efficiency of the photo-induced reactions is the separation of the radical ion pair into free radical ions. The authors suggested, in addition to the Farid and Mataga hypothesis [80–83], that this separation could be facilitated by the addition of some additives thereby stabilizing the corresponding radical cations. A plausible complexation between dioxolane radical cations and aromatic substrates, in a fashion similar to that reported by Majima, Pac, et al. [168, 169], was suggested. A similar explanation was also presented to account for the catalytic effect of the salts, although, differently from aromatic hydrocarbons, they do not affect the fluorescence of singlet excited DCA. In fact, metal-salts-modified reactions still occur faster than in their absence, showing quantum yields in the range 2.8–5.8. These latter values, excluding on the basis of experimental proofs the involvement of singlet oxygen, strongly support a chain electron-transfer mechanism, at least in competition with Foote's classical proposal [84]. The inhibition observed in the presence of TEA and/or DABCO can be explained as previously reported [111]. However, a more detailed mechanistic study has been reported, nearly simultaneously, in the Schaap and Griffin's groups [102, 105]. Schaap and co-workers found that the DCA/BP cosensitized photooxygenations of epoxide 69a, and/or diphenyl sulfoxide 81a are totally inhibited by BQ, maintained at sufficiently high concentration level (10^{-2} M), to allow efficient trapping of superoxide ion [102]. *Viceversa*, the DCA/BP photooxygenation of 74a is only slightly modified upon the addition of BQ, since the corresponding 1,2-dioxolane, 76a is formed as usual. These important results support further confirmations that the BQ action in DCA-sensitized reactions is strictly related to the peculiar chemical properties of the substrates and to those of their corresponding radical cations. Furthermore, the TCA/BP photooxygenation of 74a, conditions in which 69a, and/or 81a are completely recovered, leads, although slowly, to the corresponding 1,2-dioxolane 76a. These experimental proofs further support the involvement of a chain electron-transfer radical cation mechanism, as previously described in Mizuno's report [104].

Griffin's group [105], demonstrated the formation of ozonides by electron-transfer photooxidation of small-ring cycloalkenes, a further significant achievement to the mechanistic pathways involved in these processes.

Several polymethyl-1,2-diphenylcyclobutenes, 82a–c, subjected to DCA-photooxidation in acetonitrile, afford 1,4-diketones 83a–c together with moderate amounts of the ozonides 85a–c, apparently formed from oxiranes, 84a–c, produced in the primary step:

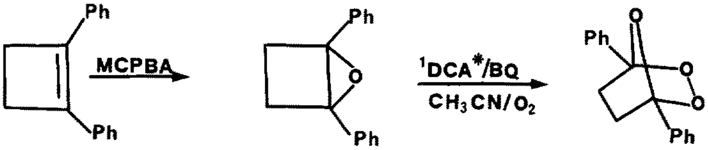


(38) (39)

82a: R′ = R″ = H; 82b; R′ = H, R″ = CH_3; 82c: R′ = R″ = CH_3

Contrarily to an initially incorrect conclusion, reached on the basis of recommended, albeit low, concentrations of BQ, with an enhanced concentration level of this additive, the observed oxidations are completely suppressed and the only products observed are the ring-contracted derivatives 86a–c as reported in Eq. (39).

These results suggested that superoxide ion is indeed involved as a reactive intermediate, at least in the electron-transfer processes, leading to 1,4-diketones and oxiranes, whereas the ring-contracted derivatives arise from a process not requiring superoxide ion as the oxygen reactive species. In this regard, a comparative study on the sensitized photooxidation of the same substrates with singlet and/or triplet excited sensitizers confirmed that the ring-contracted derivatives arise from a singlet oxygenation of the substrates, through the formation of unstable endoperoxide derivatives, which are rapidly converted into cyclopropanes derivatives [Eq. (38, 39)]. In light of the DCA-sensitized process, the opposite conclusions of Sakuragi [183] (that superoxide ion is still involved, even in the methylene blue-sensitized endoperoxidation of cyclobutenes), cannot be operative in this latter case. More interestingly, in the same paper the authors, in dealing with the DCA-sensitized photooxidation of several epoxides, (prepared through *m*-chloroperbenzoic acid oxidation of the corresponding cyclobutenes, 82a–c), observed the formation of the corresponding ozonides, together with benzoic anhydride, even in the reactions carried out in the presence of BQ (ca. 10^{-2} M):



(40)

Thus, a pathway in which superoxide ion is not required for the conversion of epoxides to ozonides, on the contrary to Schaap's suggestion, would exist.

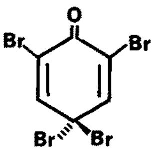
Actually, these latter results constituted further experimental proof supporting Schaap's hypothesis. These latter oxiranes, in fact, exhibit a behavior strikingly different from that of the *cis*- and *trans*-stilbene oxides because they efficiently quench the ^{1}DCA fluorescence with the concomitant formation of the radical ion pair.

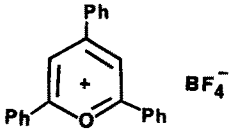
5 Sensitized Chain Radical-Cation Electron Transfer Processes

During the 70s, Barton [125, 138], Landis [184], and Tang [140] proposed a new pathway for the sensitized photooxygenation of several classes of unsaturated organic compounds alternative to the singlet and Foote-type oxygenations, in which the radical-cation intermediates react with triplet oxygen and propagate a chain oxidation. However, to better investigate these sensitized reactions leading to the oxidation products through a chain electron-transfer mechanism, it was desirable to use sensitizers which neither produce superoxide ion, nor singlet oxygen. for this purpose TCA [99], 2,4,6-triphenylpyrylium tetrafluoroborate (TPP^+BP4^-) [185], and 2,4,4,6-tetrabromocyclohexa-2,5-dien-1-one, TBCHD [90, 112], were found appropriate sensitizers.

In the $TPP^+BF_4^-$-sensitized photooxygenation of 21, leading to the corresponding thermally stable 1,2-adamantylideneadamantane dioxetane, 23, direct evidence for the chain electron-transfer reaction was achieved by quenching experiments, *ns* laser flash photolysis, and cyclic voltammetric studies [185].

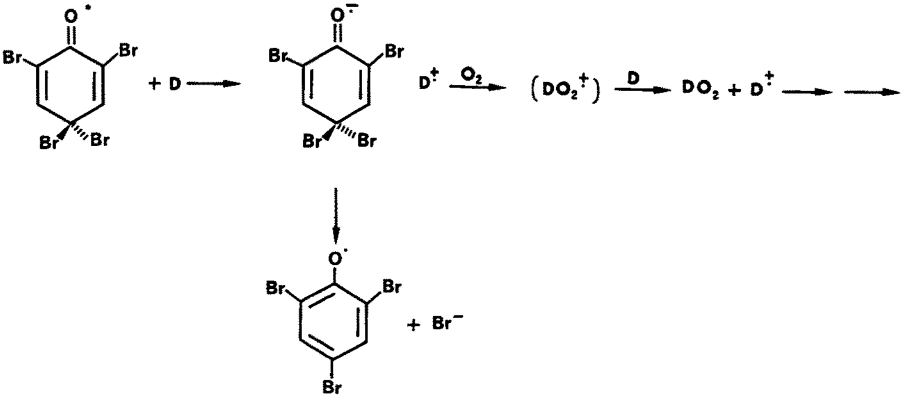
In fact, the addition of 1,4-dimethoxybenzene (DMB) (0.13 equiv.), easier to oxidize than 21, appreciably quenches the reaction. The laser flash photolysis with a nitrogen-pulsed laser (337 nm) of a $TPP^+BF_4^-$ (1.6×10^{-4} M) dichloromethane solution, in the presence of 21 (6.2×10^{-2} M), conditions in which nearly 80% of the singlet excited sensitizer (E^{red} = 0.29 V vs SCE) is quenched by 21, gives a transient absorption (Λ_{max} 550 nm) assigned to a pyranil radical $TPP^{\cdot}$.





From the decay kinetics of the 550-nm band, in the absence and presence of oxygen, the rate constant for the process pyranyl radical $TPP^{\cdot}$ plus oxygen can be estimated to be ca. 10^7 dm^3 mol^{-1} s^{-1}. This latter result shows that $TPP^{\cdot}$ is far less efficient in generating superoxide ion than several cyanoaromatic radical-anion sensitizers. Finally, cyclic voltammetric experiments, under oxygen atmosphere, clearly show that the reversible CV curves, recorded for the sensitizer under inert atmosphere, become totally irreversible. This typical EC behavior [185] had also been observed in a case previously reported [186].

Cationic sensitizers, such as pyrylium and/or trityl salts, having strong absorption in the visible region, can also induce, through an electron-transfer process, cycloreversion reactions in cage molecules and cyclobutane derivatives [187, 188]. TBCHD, usually used as a mild and selective brominating agent [189, 190], acts as an electron acceptor in the sensitized photooxygenation of several unsaturated organic substrates such as 8, 10a, 22a, 25, 64a [90, 111], affording reaction products similar to those previously reported by Foote [84], Farid [99], and Schaap [98] in the DCA-sensitized reactions on the same substrates. The exceedingly low reduction potential (E^{red} = 0.29 V vs SCE), together with its excitation energy



Scheme 14

(ΔE_{0-0} = 2.94 eV) and the oxidation potentials of the donors substantiate, on the basis of Weller's equation [59], that an exothermic electron-transfer process between the donors and the singlet excited sensitizer ^{1}TBCHD* is in agreement with the physical properties of the reagents [90, 111]. The TBCHD-sensitized reaction conditions closely resemble the methylene blue (MB^+)-sensitized photooxidation of 10a [124], a case in which the reduced sensitizer is unable to reduce molecular oxygen to superoxide anion. The driving force appears to be the aromatization of the intermediate radical anion ($TBCHD^{\bar{\cdot}}$) into tribromophenoxyl radical and bromide ion, which, by suppressing the back electron-transfer process, allows the free radical cations to react with molecular oxygen, as in Scheme 14.

Interestingly, as reported in the previous section, two unconnected mechanisms seem to operate in the TBCHD-sensitized photooxidation of several substituted 2,3-diaryl-5,6-dihydro-1,4-dioxins 22a–c, and substituted 2,3,5,6-tetraphenyl-1,4-dioxin, 64a–d, yielding, as major products, 1,2-ethanedioldibenzoates 24a–c, and (*Z*)-stilbenediol dibenzoates 66a–d respectively, together with variable amounts of the corresponding α-diketones [90, 111] (Eqs. (27)].

On the contrary to the DCA-sensitized conditions, where superoxide is involved as the reactive oxygen species, the TBCHD-sensitized reactions, as expected, are not quenched by BQ, an efficient superoxide ion quencher. In fact, no superoxide ion can be formed in the medium, owing to the highly unfavorable electron-transfer process from the radical anion ($TBCHD^{\bar{\cdot}}$) to molecular oxygen (endothermic by 1.21 eV).

In spite of the encouraging results obtained in the TBCHD-sensitized photooxygenation of several unsaturated substrates, however, this procedure suffers a severe limitation fundamentally due to the thermally and/or photochemically low stability of the sensitizer. The photoreactions of different cyclohexadienone derivatives have been widely studied by Schuster and co-workers [191–192].

In this regard, a similar nonaromatic electron acceptor, namely 2,3,5,6-tetrachloro-*p*-benzoquinone, TCB, (E^{red} = 0.02 V vs SCE) [91], in virtue of the higher thermal and/or photochemical stability, its exceedingly low reduction potential and its peculiar excitability in the triplet state (E_T = 50 kcal/mol), may be a useful sensitizer for the photochemical oxygen functionalization of several unsaturated and/or heterocyclic derivatives. In fact, its triplet excited state can produce singlet oxygen by energy transfer on molecular oxygen, as well as inducing an easy electron-transfer process on several donors with the generation of a radical ion pair, eventually affording different reaction products. A great deal of preliminary results, described in some communications [128], and presented at several meetings [153, 193], seems to confirm the high versatility of this electron acceptor, extensively used by Roth and co-workers to induce via an electron-transfer process different reactions on simple olefins and strained organic compounds [194–197].

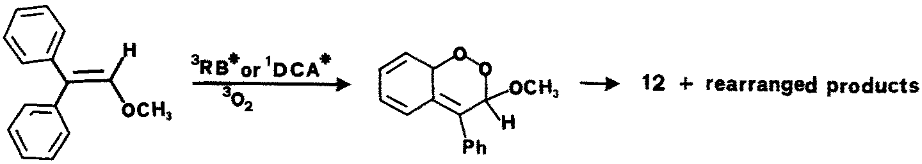
Because of the low reduction potential of TCB, the energy content of the radical ion pair resulting from the reaction of triplet excited sensitizer ^{3}TCB* and many olefins is insufficient lead to the triplet state of the olefins. In this case the isomerization takes place via a chain radical-cation mechanism [194, 195]. The same electron acceptor also induces the electron transfer-sensitized valence isomerization of quadricyclane to norbornadiene [196, 197].

Detailed characterizations by laser flash photolysis of the transient radical-ion species involved in these processes have also been reported by Haselbach, Mattay, Rentzepis, and their co-workers [72, 198–199].

6 Cyanoaromatic-Sensitized Reactions Involving Singlet Oxygen

The cyanoaromatic-sensitized electron-transfer photooxygenation (Foote-type) is a useful preparative reaction with a very limited class of unsaturated olefins, namely those substituted by aromatics and, at the same time, totally inert towards singlet oxygen. On the other hand, in the previous sections, it has been many times underlined that electron-transfer reactions may compete with singlet oxygen formation and, above all, that the reactions of $^1O_2$ may be the only observable outcome in the presence of singlet-oxygen acceptors.

Some years ago, Foote and Mazur reported [200] the singlet oxygenation of 1,1-diphenyl-2-methoxyethylene 88 (DPME) yielding, through a [1 + 4]-cycloaddition reaction, the corresponding endoperoxide, 89, whose decomposition, on warming, led to a complex mixture of products together with benzophenone 12:



88 89

(41)

Further detailed studies on the singlet oxygenation of the same substrate, performed by a Japanese group [201], compelled Foote et al. to reinvestigate this process, with the reassignment of the structure of one previously reported compound, and the characterization of several other products not previously described [202]. At the same time, they confirmed that, with the exception of benzophenone, all of the rearranged products derived directly from the decomposition of the initial endoperoxide 89. Surprisingly, the same authors [135] also observed that the DCA-sensitized photooxygenation of the same substrate afforded a product mixture similar to that formed on RB sensitization. The only difference was that significant amounts of benzophenone (5–50%) were formed along with the other products. However, when TS was present in high concentrations, such that the photooxygenation of DPME could proceed by way of an indirect mechanism [135], benzophenone formation was greatly enhanced (95%).

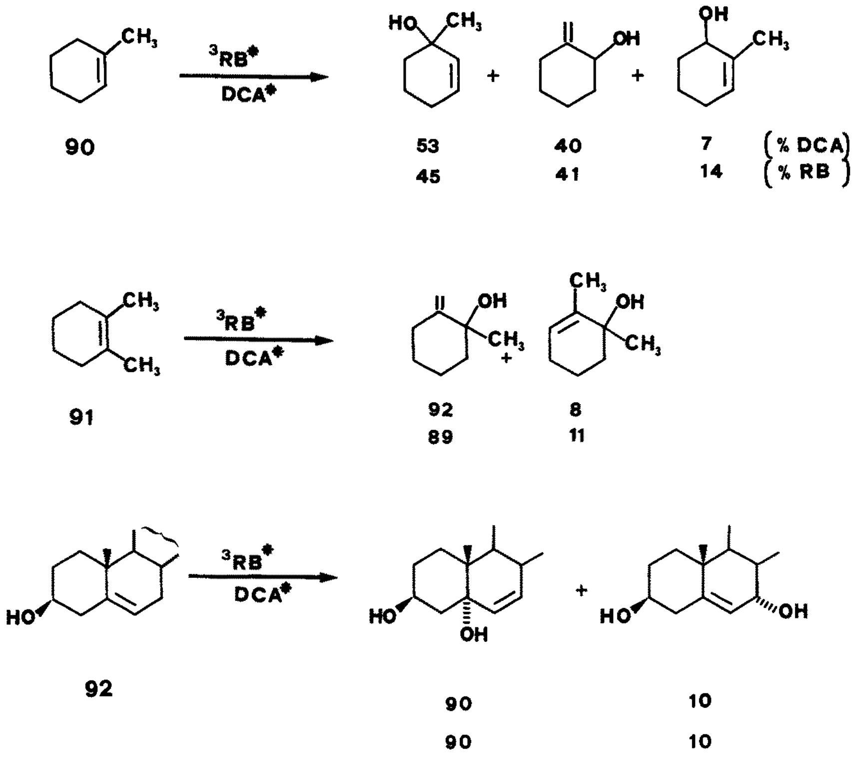
Having ruled out the hypothesis that benzophenone could derive from the intermediate endoperoxide 89, the authors suggested that the direct route must afford mainly singlet oxygen products; instead, when the ratio TS/DPME increased, the fraction of singlet oxygen products decreased, favoring an electron-transfer process in which the radical-cation intermediate ($DPME^{+\cdot}$), indirectly formed, reacted with superoxide ion. In other words, these results clearly show that in the DCA-sensitized photooxidation of specific substrates, the singlet oxygen pathway may compete with the electron-transfer process. This first hint, that singlet oxygen could be a singificant product from the cyanoaromatic-sensitized reactions, was supported by spectroscopic data [204]. In fact, flash photolytic studies on the reaction of *trans*-stilbene with DCA under nitrogen atmosphere, in polar solvents, and/or in the presence of various additives, reveal, in addition to the well-known absorptions of radical cation (TS^{+}) at 473 nm and radical anion $DCA^{-\cdot}$) at ca. 580 nm, a shoulder at ca. 440 nm, very close to the known absorption of triplet excited sensitizer ${}^3DCA^*$ [203–205]. More interestingly, this band shows the same absorption maximum regardless of the substrates. In their studies, the same group reported that the most efficient production of the triplet transient absorption can be envisaged when singlet excited cyanoaromatic sensitizers are quenched by substrates containing a heavy metal such as iodoxylene. Under these conditions, intersystem crossing (*i.s.c.*) can be rapid and an efficient energy-transfer reaction between triplet-excited sensitizer ${}^3DCA^*$ and triplet molecular oxygen can afford singlet oxygen, easily trapped by substrates such as 2-methyl-2-pentene. The quantum yield of direct *i.s.c.* of triplet-excited sensitizer is proportionally reduced if singlet-excited DCA undergoes other faster reactions, and/or a quenching deactivation process. In order to determine the occurrence of energy-transfer processes, such as those reported in Eqs. (42, 43), the same group studied the intensity of the singlet-oxygen emission, monitored at 1.27 μm, by comparison with that produced with other sensitizers of known quantum yields of singlet oxygen production [204–206].

$${}^1DCA^* + {}^3O_2 \longrightarrow (DCA\cdots O_2) \longrightarrow DCA + {}^1O_2 \qquad (42)$$

$$\begin{tikzcd} {}^1DCA^* + {}^3O_2 \arrow[r] & {}^3DCA^* + {}^1O_2 \arrow[d, "{}^3O_2"'] \\ & DCA + {}^1O_2 \end{tikzcd} \qquad (43)$$

They found that singlet oxygen production is a function of oxygen concentration and measured a quantum yield close to 2. Thus, a double energy-transfer process, as in Eq. (43), seems to be the major mechanistic pathway for singlet oxygen production. Cyanoaromatic-sensitized photooxygenation of single olefins, such as 1-methylcyclohexene, 90, 1,2-dimethylcyclohexene, 91, cholesterol, 92, and several others [119], afford complex reaction mixtures, indistinguishable from those obtained in the singlet oxygenations of the same substrates [207] (Scheme 15).

To characterize these reactions, a series of kinetic investigations were carried out, and the dependence of product yields on solvent polarity, oxygen, and substrate concentration were determined. Compounds 90–92 react, at appreciable rates, in benzene as well as in acetonitrile and this behavior is clearly insonsistent with an electron-transfer mechanism. On the other hand, compounds 90–92 exhibit solvent isotope effects in close agreement with those expected for a singlet oxygen mechanism. Finally, the quantum yields of product formation are close to the values expected for a singlet oxygen reaction.



Scheme 15

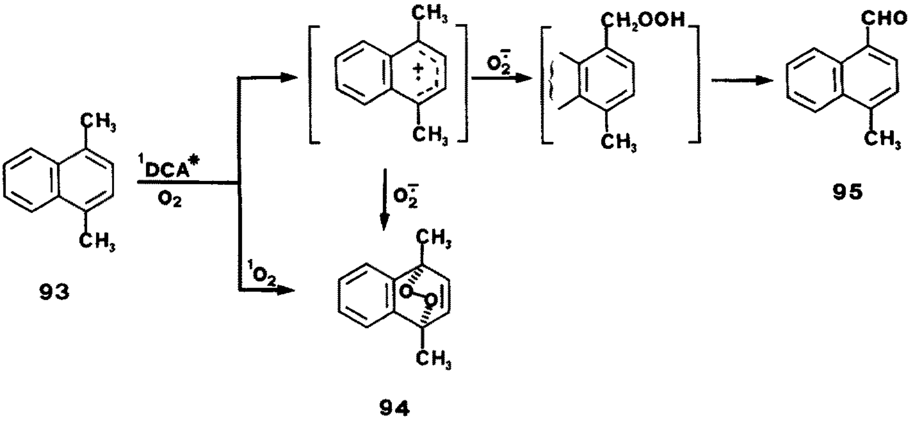
In light of these experimental data, it seems rather strange that the kinetics of DCA fluorescence quenching are consistent with an electron-transfer process [207]. Several possible explanations can be advanced for the apparent lack of radical ion chemistry in this system. The most likely one is that electron-transfer quenching between singlet excited $^1DCA^*$ and the olefins are immediately followed by back electron-transfer processes, making the primary process no productive. In other words, with substrates which can undergo electron-transfer to give radical ions, the radical ion mechanism will predominate at high substrate and low oxygen concentrations. Viceversa, with substrates which can undergo only singlet oxygen reactions, the mechanism will become efficient at high oxygen and low substrate concentrations. Higher substrate concentrations may also quench the excited sensitizer and this process appears to be the major cause of the observed curved plots of product formation vs substrate concentration.

Albini et al. [208] came to the same conclusions studying the photooxygenation of simple alkenes such as 2,3-dimethyl-2-butene in the presence of different cyanoaromatic sensitizers.

The results of these studies emphasize that compounds which can react with cyanoaromatic sensitizers, both by electron-transfer mechanism and by singlet oxygen reactions, are likely to show a very complex mechanistic outcome not easy to predict in advance. Anyway, if no reasonable doubts exist about singlet oxygen involvement in the cyanoaromatic sensitized oxygenations, there are some problems regarding the mechanism of its production.

Since 1981 Santamaria has been reporting that the DCA-sensitized photooxygenation of certain aromatic compounds proceeds by two distinct mechanisms, each one beginning by an electron-transfer process [113, 209, 210]. In the first one, superoxide ion is involved, and in the second one singlet oxygen, produced through an unusual process, is the active oxygen species. In the same communication the author reported that several dinitro aromatic derivatives may behave as electron acceptors in solvents such as acetone or tetrahydrofuran.

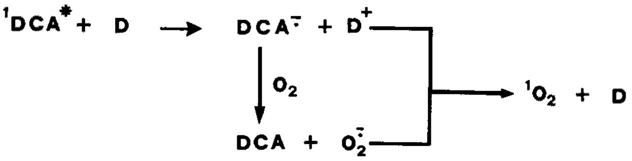
The DCA-sensitized photooxygenation of 1,4-dimethylnaphthalene, 93, in acetonitrile, afforded a mixture of endoperoxide 94, (65%) and aldehyde 95, (25%), whereas in nonpolar solvents, as well as in the dye-sensitized (MB, RB) photooxygenations of the same substrate, 94 was the only reaction product [211, 212] (Scheme 16).



Scheme 16

In order to rationalize these experimental results, the author suggested a mechanism involving a preliminary electron-transfer process between the singlet excited sensitizer and the donor, with the generation of a radical-ion pair. Subsequent trapping of the radical cation by superoxide ion would afford the corresponding endoperoxide 94 as the main reaction product in the singlet oxygenation of the starting material, as well as the aldehyde 95. Since the latter product cannot be formed via singlet oxygenation of the aromatic substrate, the author suggested the involvement of an unstable hydroperoxide intermediate, directly formed by irradiation of the starting material [213], and/or by reaction of the intermediate radical cation with superoxide ion.

As a consequence of several quenching results, the author claimed for the singlet oxygen formation a different mechanism to that advanced by Foote. In fact, no oxygenated products were observed in the presence of reducing agents, such as sodium borohydride and triphenyl posphine, whereas in nonpolar solvents or with triplet excited sensitizers, the same reducing agents did not affect the photochemical reactions, leading quantitatively to the corresponding endoperoxide. This latter experimental observation induced the author to suggest a stepwise formation of singlet oxygen, requiring a preliminary electron-transfer process (Scheme 17).



Scheme 17

In the last paper on this topic [113], the same group extended this study to several different unsaturated organic compounds, leading to the conclusion that the DCA-sensitized photooxygenation of electron-rich donors is affected by solvent polarity. The chemical outcome can be connected with the fluorescence data and the formation of superoxide ion, and/or singlet oxygen proceeds from a charge-transfer complex between the donor and the acceptor upon excitation.

An interesting piece of work on the photochemically induced oxygenation of methylbenzenes, bibenzyls, and pinacols in the presence of naphthalene-1,4-dicarbonitrile as cyanoaromatic sensitizer, has been recently published by Albini and Spreti [214]. In this paper, the authors in discussing the mechanisms of these reactions on the basis of product distribution and quantum yields, both in the absence and in the presence of oxygen, suggested a preliminary electron-transfer process from the donors to the singlet excited sensitizer, followed by different reaction pathways in relation to the donor. In fact, methylbenzene and/or some bibenzyl radical cations undergo an easy deprotonation, whereas pinacol radical cations undergo a carbon-carbon cleavage followed by reaction of the benzyl radicals with oxygen.

Methylbenzene photooxidations can also be sensitized by DCA [215], and preliminary data on the sensitized photooxidation of bibenzyls and pinacols have also been reported by Griffin et al. [216–217].

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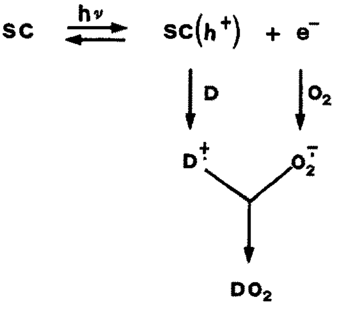
7 Semiconductor-Induced Photooxygenations of Organic Substrates

Increasing recognition of the importance of photoinduced electron-transfer reactions in synthetically useful transformations has led to an intense investigation of various methods of redox reactions of organic substrates. As previously reported, the control of photoinduced electron-transfer reactions between donors and acceptors (see Scheme 2) requires the diffusion apart from the primary geminate pair of the corresponding radical ions, so that the subsequent dark reactions of the oxidized and reduced species can be more easily studied. Significant achievements towards this critical prerequisite have been made, either by rationalizing (for the reactions taking place in homogeneous solution) the effect of distance, solvation, exothermicity, and orbital orientation on the forward and backward rates [2, 66], or by using alternative chemical procedures in which redox reactions, initiated by absorption of a photon at the surface of an electrode, allow the physical separation of the radical ions [218]. The salient features of this procedure, i.e., "organic photoelectrochemistry", well described in a series of excellent reviews [219–220], have been applied to semiconductor powders: photocatalysts responsive in the visible and ultraviolet regions as sites for initiating and controlling reactions on several classes of organic compounds, such as alcohols, phenols, olefins, alkyl aromatics, sulfides, lactams, and amines [221–229].

Semiconductors are characterized by two separated energy bands, namely, a filled low-energy valence band, and an empty high-energy conduction band. Band theory predicts that photocatalyzed oxidations or reductions on their surfaces can occur with adsorbed donors or acceptors when the redox potentials of the substrates lie between their valence and conduction bands. The band positions of common semiconductors (TiO_2, SnO_2, ZnO, WO_3, CdS, CdSe, and others) [230] and how they shift with changes in electrolyte are of great importance for our purposes [231]. In fact, the bands of TiO_2 (rutile) shift negative by about 0.7 V vs SCE by changing the solvent from water (pH 1, -0.1 V vs SCE) to acetonitrile [232]. Since the reduction potential of oxygen in acetonitrile is -0.78 V vs SCE [148], and therefore isoenergetic with the conduction band of the semiconductor, this implies that oxygen can assume the role of the acceptor with the generation



Scheme 18

of superoxide ion, which when coupled with the radical cations affords the oxygenated products (Scheme 18).

In order to account for such a mechanism, photochemical excitation of a semiconductor surface might induce the promotion of an electron from the valence band to the conduction band. Since relaxation of the high-energy electron is inhibited by the absence of intra-states, if the lifetime of this photogenerated electron-hole pair is sufficiently long to allow the interfacial electron transfer from an accumulation site to an electron acceptor, as well as the interfacial electron transfer from an adsorbed organic donor to the valence-band hole, the irradiated semiconductor can simultaneously catalyze both oxidation and reduction reactions in a fashion similar to multifunctional enzymes reactions [232].

The use of semiconductors for photoinduced charge separation is, however, limited by their instability to the operating conditions that can cause formation of a blocking layer or corrosion with consequent reduced photoactivity of the surface. This is expecially critical for semiconductors with narrow band gaps, which are easily degraded upon exposure even to visible light, but these problems can be significantly reduced, either by attaching catalysts or inert coverages or by using highly stable metal oxide with large band gaps as semiconductors whose photoactivity is generally maintained even when the size of particles decreases to the colloidal range [233]. In conclusion, regarding the interaction with light, a striking similarity exists between the orbital description of molecules and the band description of semiconductors, in spite of the apparent differences in the two systems.

8 Conclusions

In the last ten years, the enormous progress made in the field of photoinduced electron-transfer reactions, including oxygenations, would not have been possible without the combined efforts in several different chemical disciplines. In fact, the achievements in the field of modern organic electrochemistry, the development of new and more refined analytical techniques to identify and study short-lived intermediate radical ions, thermally and/or photochemically generated, the contemporary photophysical studies, constructive in understanding the mechanisms and the energetics of photochemical reactions, have played a decisive role in the solution of important synthetic problems by preparatively oriented organic chemists. In this regard, the sensitized photoinduced electron-transfer reactions, modified by inert additives such as salts, aromatic substrates, quinones, and amines are particularly promising examples of the potential of this synthetic procedure.

However, as indicated in the text of this chapter, there are many other ways of generating such radical cations, occasionally leading, under oxygen atmosphere, to reaction products similar to those obtained in the photoinduced oxygenation pathway. Although, in many instances, the different modes of evolution of radical cation intermediates, dictated by reaction conditions (solvent polarity, oxygenated or inert atmosphere, the presence or absence of other intermediates, nucleophiles, acceptor radical anions, differences in local concentrations), may generate an unaccountable confusion; however, only the full understanding of the peculiar differences in the mechanisms and energetics of photochemical and/or thermal electron-transfer reactions, including oxygenations, such as those described in this chapter, will ensure a further impulse to the research in this important area.

9 Acknowledgements

Financial support from Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione is gratefully acknowledged.

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Photoinduced Electron Transfer Polymerization

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Table of Contents

To start polymerization, reactive species which are capable of inducing the spontaneous polymerization of corresponding monomers are necessary. Photoinduced electron transfer can be used in a broad manner for that purpose. The focus of the present review is primarily directed to systems producing neutral or ion radicals, and cations or Lewis acids. Such species are the final products of a photoinduced electron transfer process either between neutral donors and neutral acceptors, or between neutral donors and positively charged acceptors. Among the numerous classes of compounds, monomers bearing electron-repelling or electron-accepting substituents can be involved in the electron transfer process. Very often, the electron transfer takes place between non-polymerizing compounds resulting in initiating species. Sometimes in such cases, the monomer molecules have a detrimental effect on the efficiency of polymerization initiation due to several quenching processes. Also, the termination steps can be influenced through the products of photoinduced electron transfer.

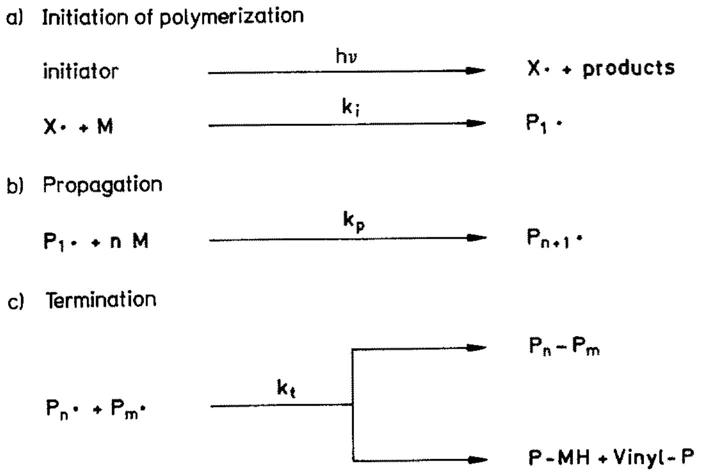
Topics in Current Chemistry, Vol. 156

1 Introduction

Recently, photopolymer systems have aroused increased interest because of their manifold applications in several high technologies [1–3]. Among such systems, those derived from photoinduced polymerization play an important role. The fundamental principles of these systems are based on the production of species X by photoreactions, which then initiates thermal reactions of low-molecular products leading to polymer or network formation: see Eq. (1). In general, these thermal reactions are associated with low activation energies (about 60 kJ mol^{-1} for free radical chain polymerization). Therefore, such processes can also occur sufficiently fast at room temperature.

$$\text{Initiator} \xrightarrow{h\nu} \text{species X} \tag{1a}$$
$$\text{X} + \text{monomer (oligomer)} \longrightarrow \text{polymer (network)} \tag{1b}$$

The photoinitiator is that component in the photopolymer system discussed which only allows the absorption of light for species X formation. The photoreaction of the initiator or the consequtive reactions of the primary photoproducts must create that species X in high quantum yields ($\phi_{in} \approx 0.5$). The photoinitiator



$$R_p = k_p(k_t)^{-1/2}[M]^{\alpha}(\phi_{in}I_{abs})^{1/2} \tag{2a}$$

$$\phi_p^r = R_p/I_{abs} \tag{2b}$$

Scheme 1

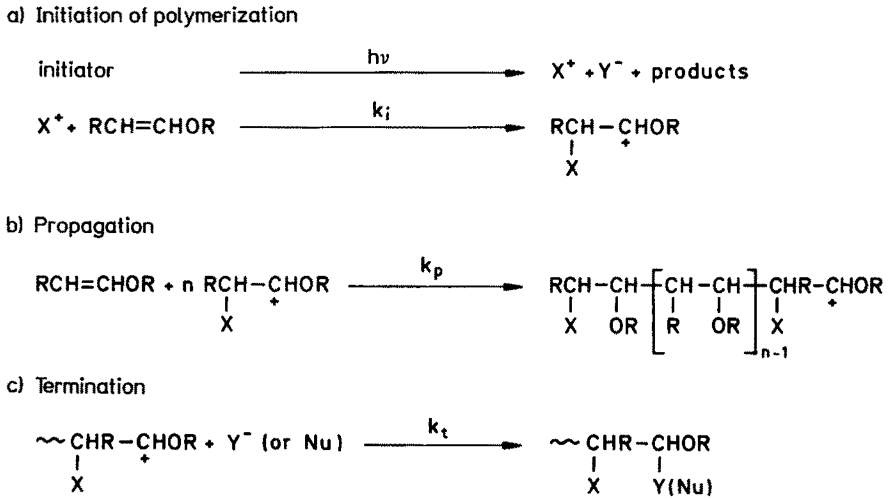
with R_p = polymerization rate; ϕ_p^r = polymerization quantum yield; M = monomer; I_{abs} = light intensity absorbed by the system.

can consist of a sole product or of a product formulation. Sometimes, monomer molecules participate in the general reaction (1a) either as the light absorbing component or as reaction partners.

Depending on the identity of the intermediates X produced one can distinguish:
- radical photoinitiators (creation of radicals; see Scheme 1) [4, 5, 6]
- cationic photoinitiators (formation of Brønsted or Lewis acids; see Scheme 2) [7–9]
- anionic photoinitiators (production of anions) [10]
- photoinitiators for concurrent radical and cationic polymerization (both radical and cation formation) [11]

A photoinduced electron transfer (PET) can be involved in the initiation of both radical and cationic polymerization. Two fundamental principles exist:
- the electron transfer takes place in the excited states (direct PET),
- the electron transfer takes place in dark reactions between products of the photoreaction and donor or acceptor present (indirect PET).

In this paper, the relevant recent literature for radical and cationic systems will be discussed comprehensively. But, only such papers have been considered, which deal with the subject of polymerization.

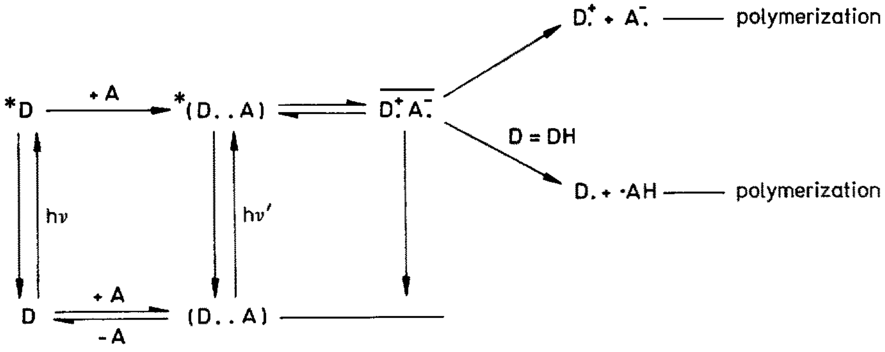


Scheme 2

2 Photoinduced Electron Transfer Between Monomer Molecules

A simple example of photopolymerization based on PET is realized, if the monomers polymerized are the electron donor (D) and electron acceptor (A) themselves [12]. Therefore, the electron densities of both compounds must be very different. With vinyl monomers, combinations of donor and acceptor substituted olefins are especially suitable systems.

A general scheme of the reaction pathways is given in Scheme 3 [10, 13]. The exciplex formation can occur in two ways: (1) excitation of the donor monomer (or alternatively the acceptor monomer) and interaction of its excited states with the opposite monomer; (2) formation of a ground-state charge transfer complex (CT) and its excitation. Mainly, because the electronic properties of the monomers used differ, the latter case is met. The ion radicals formed via PET are capable of undergoing several consequtive reactions: (1) A simultaneous ionic polymerization is possible; the donor monomer can be polymerized cationically and the acceptor monomer anionically. (2) A copolymerization between both monomers can occur. (3) A fast in-cage or out-of-cage proton transfer is possible between the cation radical and anion radical leading to neutral radicals. But, this reaction requires special structural conditions in the monomers.

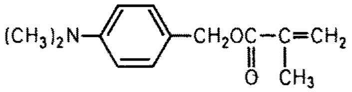


Scheme 3

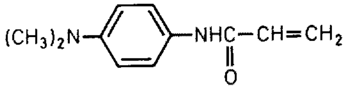
Usually, all reactions forming the initiating species must compete with various deactivation reactions.

Owing to the great number of monomers with different electronic densities, a high potential exists for that type of photopolymerization. Surprisingly, only few examples have appeared in the literature, so far.

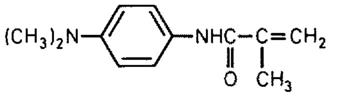
A very interesting case of the phenomenon discussed is realized by monomers, which contain both electron donor and electron acceptor moieties in their molecule. Typical products are [13, 14]:



dimethylaminobenzyl methacrylate (I)



dimethylaminophenyl acryloamide (II)



dimethylaminophenyl methacryloamide (III)

In these compounds, the double bond of the vinyl group acts as the electron acceptor, whereas the aromatic amino group functions as the electron donor. Therefore, by excitation an electron transfer can occur from the excited aromatic amino group to the double bond.

Indeed, the usual fluorescence of the isolated aromatic amines (e.g., *N,N*-dimethylaniline, DMA) is quenched by excimer formation in compounds I and II. In the process of prolonged irradiation of I and II solutions the emission intensity increases gradually because of the loss of the C=C double bonds in the system due to the polymerization reaction. A polar environment favors the charge transfer and, therefore, the fluorescence quenching of the monomer is drastically decreased, whereas the polymer formation increases.

In contrast, the monomer III cannot be polymerized by photoirradiation. In this case, the methyl group makes the double bond more electron-rich and the intermolecular hydrogen bond between the amide group and the nitrogen atom decreases the electron donor ability of the aromatic amino group.

Recently, a further example of photopolymerization of a donor-acceptor substituted monomer (methyl-2-octadecanamidopropenate) without any additive has been described [16]. The co (polyacrylates) containing electron-acceptor moieties as pendant groups are also photosensitive [17, 18]. Their photosensitivity coincides with the charge-transfer absorption band peak and, therefore, such compounds possess a photoinduced memory effect.

Among the systems with chemical different donor and acceptor molecules, the photocopolymerization between maleic anhydride (MSA), which functions as an acceptor, and electron-rich monomers has been widely investigated. As donor monomers such compounds as styrene (Sty) [19–29], cyclohexene [30], *N*-vinylcarbazole [31], 2-vinyl naphthalene [32], vinyl acetate [33], 2.4.8.10-tetraoxaspiro[5.5]undecan [34] and phenyl glycidyl ether (2,3-epoxypropyl phenyl ether, PGE) [35] have been used. In all the above cases, using high concentrations of both monomers, the absorption of the CT has been obtained in various solvents. Thus, with spectroscopic methods the complex formation constant K_{ct} can be calculated (e.g., MSA-cyclohexene $K_{ct} = 0.068\ \mathrm{l\ mol^{-1}}$ [33], MSA-tetrahydrofuran $K_{ct} = 0.33\ \mathrm{l\ mol^{-1}}$ [36]), and a selective excitation of the CT is possible in many cases.

The general pathways outlined in Scheme 3 are obeyed in all systems with MSA as acceptor A. In Sty-MSA system, the expected radicals Sty^{+} and $\mathrm{MSA}^{\overline{\cdot}}$ have been detected by ESR [25] and flash photolysis measurements [26, 28]. In that system, by laser excitation with $\lambda = 368.8$ nm the yields of copolymers depend on the polarity of the solvent used (46.9% in CH_2Cl_2, 16.6% in dimethyl formamide, 1.4% in toluene). Studies of the kinetic behaviour of photocopolymerization of MSA with vinyl acetate showed that the velocity of this reaction decreases with the increase of either the reaction temperature or the solvent polarity. With this system some hints point to the participation of triplet radical pairs, because the copolymerization rate decreases with isoprene addition ($E_T \approx 240\ \mathrm{kJ\ mol^{-1}}$, $E_T(\mathrm{MSA}) \approx 300\ \mathrm{kJ\ mol^{-1}}$).

But, the mechanism of the polymerization differs with the monomer used. In MSA-olefin systems, the fast and efficient proton transfer reaction discussed above takes place leading to neutral radicals, which then initiate the radical copolymerization. Therefore, these copolymerization reactions are retarded by the addition of free radical trapping agents (e.g. 4-hydroxy-2,2,6,6-tetramethyl piperidine-1-oxyl). In the MSA-*N*-vinylcarbazole system, as a side reaction, either cationic homopolymerization (in less basic solvents) or cyclodimerization (in moderate basic solvents) of the vinyl compound can also occur. The copolymerization of MSA and PGE is also an ionic mechanism [35].

Further examples for electron acceptor monomers are: acrylonitrile [37], diethyl fumarate [39], fumaronitrile [29, 30, 38], maleonitrile [38], *N*-carbethoxymaleimide [29], *N*,*N*-diethylaminoethyl methacrylate [39], nitroethylene [10] and *N*-ethylmaleimide [40]. As electron donor monomers also are used: vinyl alkyl ethers [38, 40], alkyl methacrylate [40], *N*-vinyl pyrrolidone [40] and cyclohexene oxide [10].

As follows from the data given above, the potential possibilities of PET between monomer molecules as a tool for polymerization initiation have not been exploited so far. Also, some fundamental questions of the detailed mechanism are unclear.

3 Intermolecular Photoinduced Electron Transfer Between Monomer Molecules and Donor or Acceptor Molecules

As discussed above, monomer molecules are capable of functioning either as π-electron donors and π-electron acceptors (e.g. C=C double bond containing compounds), respectively, or as *n*-electron donors (e.g. epoxides). Therefore, their ground or excited states can interact with donor or acceptor molecules, which are unable to polymerize. For that interaction the general Scheme 3 holds, too. Clearly, in these cases only a homopolymerization of the monomer used takes place. The mechanism of that reaction depends on the electronic properties existing (e.g. monomer acts as donor or acceptor), and on the structural conditions in both molecules. Again, in some cases a proton transfer reaction could occur.

The latter mechanism is met in amine-vinyl monomer systems [41–46] (see Scheme 4). Due to the small π-acceptor ability of normal substituted vinyl monomers, an interaction in the ground-state level does not take place. The exciplexes assumed are detectable in aromatic amine-acrylonitrile (AN) systems by their emission spectra, as is shown in Fig. 1 for typical examples. The emission bands at 350 nm (by *N*,*N*-dimethyl-*p*-toluidine (DMT)) and 370 nm (by *p*-phenylene diamine (TMPD) result from the normal fluorescence of the isolated amine. As can be seen, the intensity of the exciplex emission is much higher in the DMT-AN system. This corresponds to the higher polymerization efficiency of that system (ϕ_p^r by $\lambda = 313$ nm and 80 K: 0.6 for DMT; 0.15 for TMPD [46]). Mainly, the much higher dipole moment of DMT (1.1 D) is responsible for this result. The cation radicals [46] or neutral radicals [42] of the amines formed after PET and proton transfer have been detected by ESR measurements. As expected, the rate of photopolymerization of the systems discussed increases with increasing

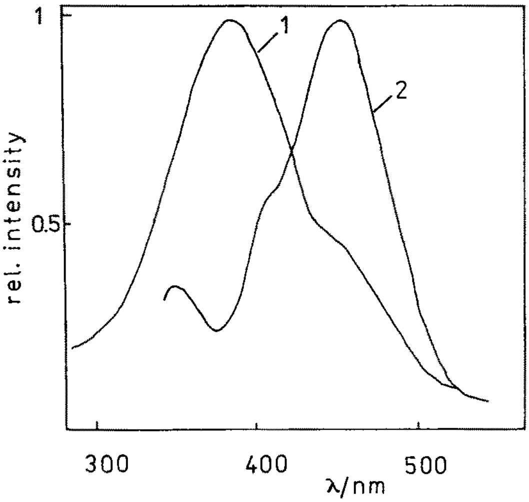


Fig. 1. Emission spectra of *p*-phenylene diamine (*1*) and *N*,*N*-dimethyl-*p*-toluidine (*2*) in frozen acrylonitrile (temperature 80 K)

of amine concentration (see Fig. 2). The activity of aniline derivatives initiating photopolymerization of AN decreased in the order tertiary amine > secondary amine > primary amine, and the activity is higher as the size of alkyl groups on the nitrogen atom increased.

1-Benzyl-1.4-dihydronicotinamide (BNAH), a model for NDAH (nicotinamide dinucleotide coenzyme), photopolymerize methyl methacrylate (MMA) easily and Sty more slowly. However, surprisingly, the polymerization of AN cannot be initiated with this amine [47, 48]. The copolymer composition curves of MMA and Sty in dichloromethane and methanol suggest a radical mechanism corresponding to Scheme 4. Also, both the results of kinetic studies ($R_p \approx [BNAH]^{1/2}$; number average degree of polymerization $P_n \approx [BNAH]^{1/2}$) and the results of the fluo-

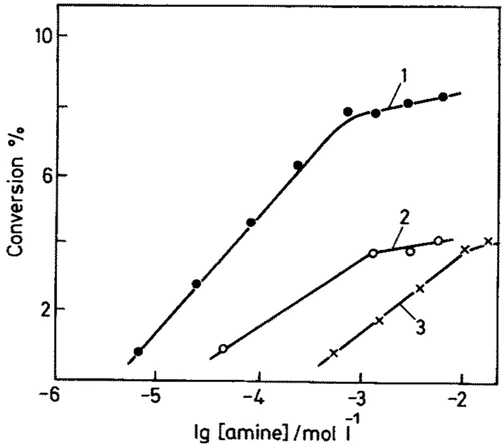
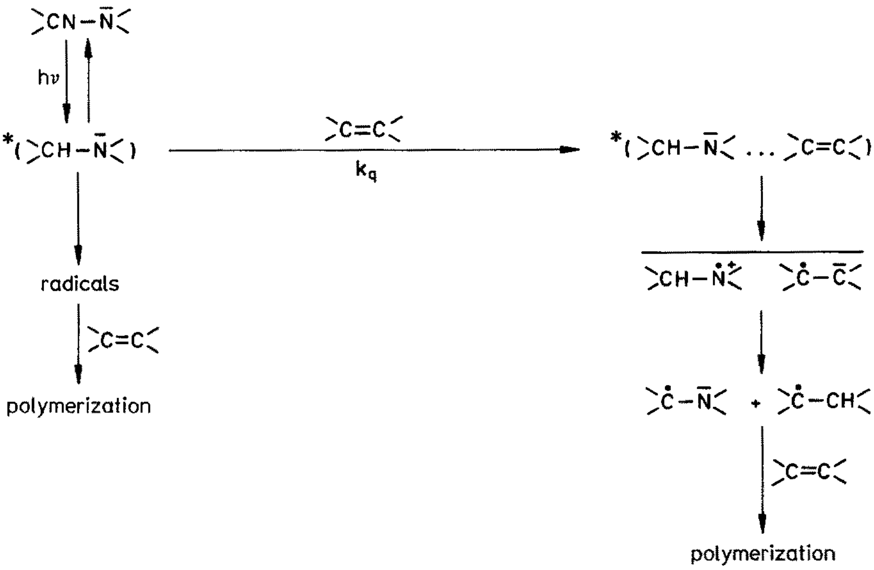


Fig. 2. Monomer conversion by the photopolymerization of acrylonitrile with aniline derivative (1: *N*,*N*-dimethylaniline, 2: *N*-methylaniline, 3: aniline) in dependence of amin concentration (in dimethylformamide, at 30 °C, [acrylonitrile] = 4.88 mol l^{-1}, $\lambda > 320$ nm of 400 W high-pressure mercury lamp, irradiation time 60 min)

rescence quenching of BNAH with all three monomers support this assumption. At high concentrations of BNAH, both R_p and P_n of MMA photopolymerization are remarkedly decreased, because of BNAH contribution to the termination steps of the chain reaction.



Scheme 4

However, the polymerization results of the above systems must be examined very carefully. If not all excited amine molecules are quenched by the vinyl monomers, then the known homolytic bond cleavages of the amine molecules also lead to radicals capable of polymerization initiation (see Scheme 4). This could be possible with monomers possessing only very weak π-acceptor ability.

Furthermore, anilines can act as a sensitizer for the photoinduced phenol addition at PGE [49]. So far, the detailed mechanism of that reaction is unclear. But, the formation of coloured by-products by DMA sensitization points to the involving of PET steps.

Such polycyclic aromatic hydrocarbons as anthracene or heteroaromatics as acridine, phenazine and 2,4,5-triphenyl oxazole act as π-donors for the π-acceptors AN and alkyl methacrylates [50–53]. Again, the interaction of the donor excited states with vinyl monomers leads to exciplex formation. But, the rate constants (k_q^M) of these quenching processess are low compared to other quenching reactions (see Table 1). The assumed electron transfer character is supported by the influence of the donor reduction potential on the k_q^M value (see Table 1), and the detection of the monomer cation radicals with the anthracene-MMA system. Then, the ion radicals initiate the polymerization, the detailed mechanism of which is unsolved,

Table 1. Rate constants (k_q^M) for quenching of donor excited states by vinyl monomers and half wave oxidation potentials of donor ($E_{1/2}^{ox}$)

Donor	$E_{1/2}^{ox}$ (V)	Acceptor	k_q^M ($l\ mol^{-1}\ s^{-1}$)
Anthracene	−1.40	methyl methacrylate	1.3×10^7 a)
		acrylonitrile	0.95×10^7 a)
		butyl methacrylate	2.3×10^3 b)
Acridine	−1.04	butyl methacrylate	6.0×10^3 b)
Phenazine	−0.61	butyl methacrylate	7.2×10^3 b)
2,4,5-Triphenyl oxazole		methyl methacrylate	4.0×10^7 a)
		acrylonitrile	$< 10^5$ a)

a) Quenching constant of singlet state
b) Quenching constant of triplet state

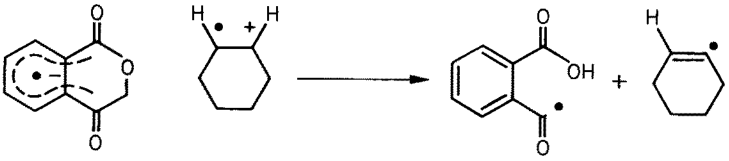
so far. In agreement with this idea, 9,10-diphenyl anthracene is unable to initiate MMA photopolymerization.

However, in hydrogen donor solvents such as tetrahydrofuran (H-A), a photoinduced reduction of the donor also can occur; see Eq. (3). Indeed, the dihydrogenated donor (donor-H_2) can be isolated from the solution. The solvent derived species A, then initiates the polymerization of vinyl monomers.

$$^3\text{donor} + \text{H-A} \rightarrow \cdot\text{donor-H} + \text{A}\cdot, \qquad (3a)$$

$$\cdot\text{donor-H} + \text{H-A} \rightarrow \text{donor-H}_2 + \text{A}\cdot. \qquad (3b)$$

Similar to the above discussed processes, the photoinitiation of the copolymerization between cyclohexene and AN in the presence of pyromellitic dianhydride or phthalic anhydride is based on the sequence of PET and proton transfer [30]. Consequently, the copolymerization rate with the former acceptor ($R_p = 1.6 \times 10^{-4}$ mol l^{-1} s^{-1}) is higher than this of the latter ($R_p = 1.4 \times 10^{-4}$ mol l^{-1} s^{-1}; [AN] = 4.5 mol l^{-1}, 30 °C). Interestingly, the average-molar weights of the alternating copolymers lie between 1000–2000 g mol^{-1}. The reason for this very small value is possibly an efficient primary radical termination due to the formation of the two radicals IV and V; see Eq. (4). Exact polymer characterization data are not available, so far.



IV V

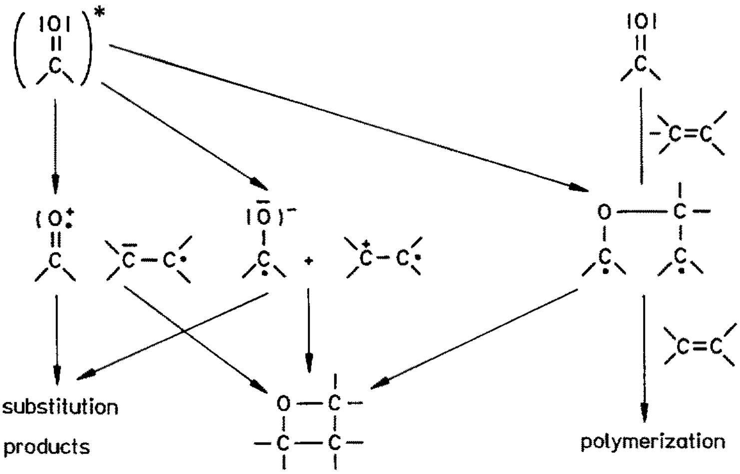
(4)

Azo bisisobutyronitrile (AIBN) can act as an electron acceptor in the photopolymerization of *N*-vinylcarbazole in benzene solution at λ = 365 nm [54, 55]. With small concentration of AIBN, a low molar weight polymer is dominant, resulting from a free radical process. But, as the AIBN concentration is raised, that low molecular weight polymer is replaced progressively by a high molecular weight fraction. This fraction is formed by a cationic mechanism starting with a PET between the excited triplet-state of the monomer as donor and AIBN ground-state as acceptor. The same situation holds with dibenzoyl peroxide as electron acceptor [56].

An electron transfer mechanism also has been reported for the interaction between excited ketones and vinyl monomers [57–61]. The olefin acts either as donor or as acceptor for the transferred electron (see Scheme 5). But, the positive free enthalpy of these reactions (ΔG_{et}), expressed by the Rehm-Weller-Eq. (5) excludes such reactions in the most cases. Furthermore, in those

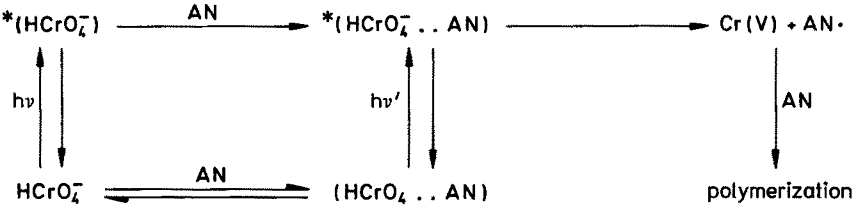
$$\Delta G_{et} = F(E^{ox}_{1/2}(D) - E^{red}_{1/2}(A) - E_{0,0} + E_{coul}) \qquad (5)$$

with $E_{0,0}$ = 0,0-energies of excited state, $E^{ox}_{1/2}$, $E^{red}_{1/2}$ = oxidation and reduction potential systems, in which a PET is thermodynamically allowed, the radical cation-anion pairs formed react to give cycloaddition or substitution products. The polymers obtained in aromatic ketone-MMA systems result from the very low initiating efficiency of 1.4-diradicals, the first products of the quenching reaction of the ketone triplet-state with MMA [62]. These diradicals decompose mainly to the initial compounds, and, therefore, the ϕ^r_p values are small (0.2–1.0).



Scheme 5

Certain inorganic salts and coordination compounds [63] are capable of a PET with monomers [64–71]. The mechanism outlined in Scheme 6 for the chromium (VI) salts-AN system can serve as a general figure for all those reactions. From



Scheme 6

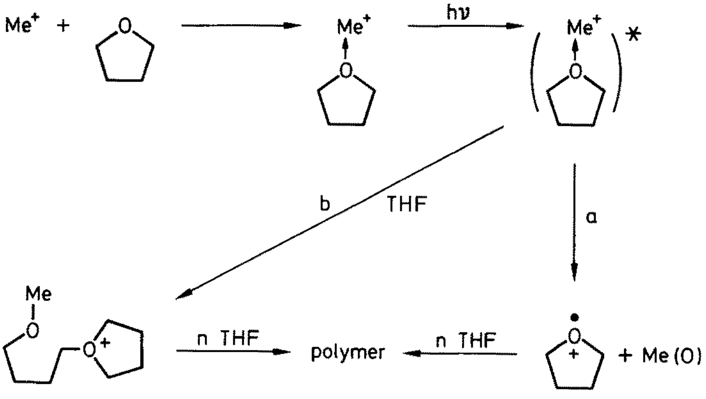
ESR experiments, it has been possible to assess that irradiation of $HCrO_4^-$ in aqueous solution in the presence of AN produces chromium (V) and an organic radical. These products are yielded from the exciplex between excited Cr(VI) and AN, which can undergo a charge-transfer reaction leading, after charge separation, to the products given in Scheme 6. Both species are able to initiate the polymerization of AN.

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad pK = 6.49 \tag{6a}$$

$$2\,HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H^+ \qquad K_d = 48\,l\,mol^{-1} \tag{6b}$$

The pH of the medium is an important parameter controlling the photoreaction; see Eq. (6). The quantum yields of chromium(VI) reduction are very low at pH > 6.0 ($\phi < 10^{-4}$ at pH 8.0) due to the equilibrium of Eq. (6). In the presence of oxygen, the formed radical AN· reacts to the far less active radical AN—OO·, which accumulates in the solution without any initiation of polymerization.

Similarly, tris(2,2'-bipyridine)ruthenium(II), [67] $Ru(bpy)^{2+}$ [70], UO_2^{2+} [68], and iron(III) salts can also be used as electron acceptors.



Scheme 7

This concept of polymerization initiation is applicable to cationic processes, too [71]; see the example in Scheme 7 for copper or silver ions (Me^+) and tetrahydrofuran (THF). A THF coordination is a prerequisite for the polymerization reaction. But, it is unclear, whether expulsion of Me(O) occurs immediately following excitation (path a) or follows the attack of the excited complex by the ground state of THF (path b).

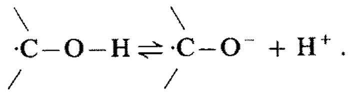
4 Photoinduced Electron Transfer in Photoinitiator Systems

In all previous examples discussed, the monomer molecules participate in the excited states reactions, which give the initiating species X. Another principle for the utilization of PET in photopolymer systems consists of the use of donors and acceptors that are independent of the monomer molecule. Then, that combination of both compounds is a "true" photoinitiator system, and it supplies the initiating species X after irradiation. This variant is more widely usable, and possesses a greater variability with respect to light absorption.

4.1 Radical Polymerization

Among the systems, which belong to this category, those containing carbonyl compounds and amines are the best investigated [72–101]. In these combinations, carbonyl compounds (aromatic or heteroaromatic ketones, quinones) are the light absorbing components. A general mechanism is given in Scheme 8.

The addition of an amine (AH) leads to a shortening of both the singlet-state and triplet-state lifetime. This life time shortening is based on a PET from the lone pair of the nitrogen atom to the carbonyl groups yielding a charge-transfer complex. In triplet charge-transfer complexes, either proton transfer (e.g. from the α position of the nitrogen) or back electron transfer or radical ion generation can take place depending on the nature of the partners and the environment. When that complex decays through proton transfer, a subsequent equilibrium of the ketyl radical ($\cdot$KH) can take place dependent on the pH of the medium; see Eq. (7)



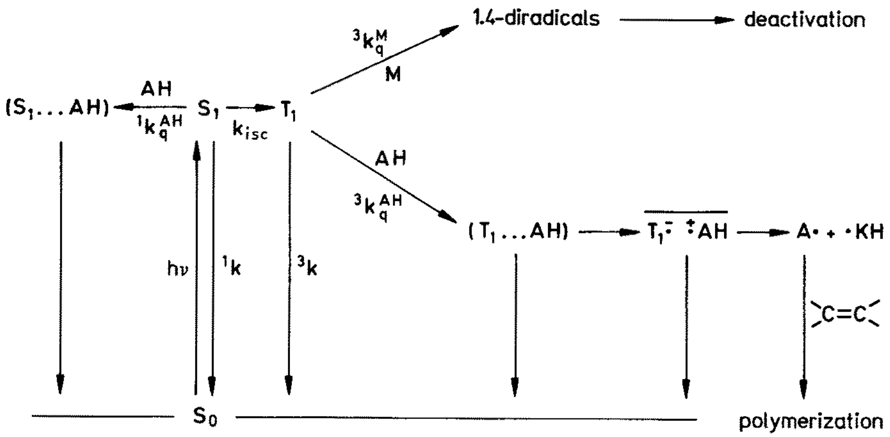
$$\cdot C{-}O{-}H \rightleftharpoons \cdot C{-}O^- + H^+ . \qquad (7)$$

Some data for the rate constants of the triplet-state quenching by amines are given in Table 2. As expected, a correlation between the ${}^3k_q^{AH}$ values and the ionization potential of the amine exists. However, the influence of the spectroscopic nature of the excited state (e.g., $n\pi^*$ or $\pi\pi^*$) is not adequately understood, so far.

Table 2. Data of the photopolymerization of methyl methacrylate with ketone-amine initiator systems (IE = ionisation potential, $^3k_q^{AH}$ = quenching constant of ketone triplet state with amine in benzene, $\Delta V/\Delta t$ = dilatometric contraction) [1]

Amine	IE (eV)	$^3k_q^{AH} \times 10^{-9}$ $(l\,mol^{-1}\,s^{-1})$	PMMA yields^e (%)	$\Delta V/\Delta t \times 10^5$ ^{e} $(cm^3\,s^{-1})$
Triethylamine	7.50		30.2^a	3.6^a
		1.3^b	28.0^b	
		2.5^c	1.1^c	
Dimethylaniline	7.14			5.0^a
		8.1^c		
		9.1^d		
Triethanolamine			11.9^a	2.7^a
			11.0^b	
			2.5^d	
tert-Butylamine	8.64	0.0046^b		

Ketone: ^{a} benzophenone, ^{b} thioxanthone, ^{c} 2-chloro thioxanthone, ^{d} fluorenone, ^{e} in bulk



S_0, S_1, T_1: ground, singlet and triplet excited state of ketone; AH: amine; M: monomer; ·KH: ketyl radical

Scheme 8

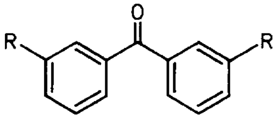
For many ketone-amine photoinitiator systems, the ketyl radicals or their anions have been obtained through flash photolysis experiments or laser spectroscopy. Also, the results of CIDNP or ESR measurements and spin trapping experiments support the reaction pathway given in Scheme 8.

With ketones in the long-lived singlet state (e.g. TX, Ac, MAc), the singlet charge-transfer complex generated by amine quenching is expressed mainly as a back electron transfer and deactivation rather than proton transfer and initiation. Therefore, such a reaction course is a loss in efficiency of the photopolymerization.

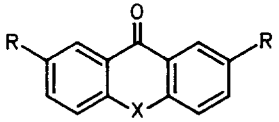
Table 3. Life times of triplet states ($^3\tau$), rate constants of self quenching ($^3k_{sq}$), of quenching with monomers ($^3k_q^M$) and of quenching with diphenyliodonium hydrogensulfate ($^3k_q^I$)

Ketone	$^3\tau$ [a] (μs)	[Ketone] × 10^4 [b] (mol l^{-1})	$^3k_{sq} \times 10^{-6}$	$^3k_q^M \times 10^{-6}$ [a,c] (mol l^{-1} s^{-1})	$^3k_q^I \times 10^{-6}$ [a]
BP	20	10	0.44	45	20
BPS	24	10		420	20
X	4.8	0.5		12000	
XS	14	1.4		430	210
TX	28	0.5	23	15	2000
TXS	109	1.1	20	0.47	150
Ac	9.2	1.0	18	0.016	
AcS	200	2.9	8	0.0022	1200
MAc	36	1.0		0.28	3500
MAcS	157	0.96	20	0.054	64

[a] Parent compound in CH_3CN, disulfonated ketones in aqueous buffer solution ($Na_2 \cdot HPO_4/KH_2PO_4$, each 1.1×10^{-2} mol l^{-1}, pH = 7), [b] ketone concentration for the measurement of $^3\tau$, [c] quenching of the parent compounds with methyl methacrylate, of the disulfonated ketones with acrylamide



R	H	SO_3^-
Abr.	BP	BPS



R	H	SO_3^-	H	SO_3^-	H	SO_3^-	H	SO_3^-
X	O	O	S	S	NH	NH	NCH_3	NCH_3
Abr.	X	XS	TX	TXS	Ac	AcS	MAc	MAcS

Also, the quantum yield of triplet-state formation (ϕ_{isc}) is depressed according to Eq. (8).

$$\phi_{isc} = \frac{k_{isc}}{k_{isc} + {}^1k + {}^1k_q^{AH}[AH]} . \tag{8}$$

Other competitive processes for the intiation reactions are the ketone self-quenching ($^3k_{sq}$), triplet-triplet annihilation and the quenching by monomers ($^3k_q^M$). Some data for these processes are listed in Table 3. Owing to the high monomer concentrations in photopolymer systems, the monomer quenching was recognized as a detrimental effect on the efficiency of the photoinitiation. In order to minimize this effect, the triplet-states must exhibit high $^3k_q^{AH}$ values as a basic condition for high radical generation. But, the polymerization reactivity of the system does not parallel the efficiency of the PET. This reactivity depends mainly on the ability of the charge-transfer complex formed to undergo proton transfer, as well as on the reaction contributing to the subsequent evolution of the radical species generated. Also, the participation of the primary formed radicals in the termination reactions of the chain process play an important role.

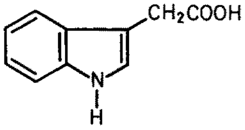
In most cases, no significant interaction between ketyl type radicals and the monomer was observed. This suggests that the amine derivative species A· is the only initiating species. In contrast, the ketyl radicals terminate the chain reaction of many monomers.

As ensues from the above discussions, the type of amine influences, in various ways, the availability of ketone-amine photoinitiator systems: during the PET, during the proton transfer, and during the addition of the α-aminoalkyl radical at the C=C double bond. For practical purposes, the compounds VI–XI possess the most favorable properties.

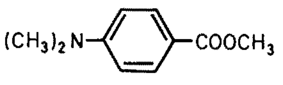
$(HOCH_2CH_2)_2NCH_3$
VI

$PhCOOCH_2CH_2N(CH_3)_2$
VII

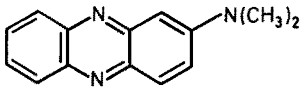
$PhNHCH_2COOH$
VIII



IX



X



XI

An interesting variant of the intiator system discussed is the combination of Michler ketone (4.4′-dimethylamino benzophenone, MK) and substituted benzophenones [103]. The triplet-state of MK (ϕ_{isc} = 0.91 in cyclohexane, 0.24 in *i*-propanol) is capable of forming an exciplex with the ground-state benzophenone. Again, similar reactions as outlined in Scheme 8 yield the Michler aminyl radical and diphenyl ketyl radical. Owing to their favorable light absorption up 350 to 430 nm, and the efficient radical formation, these combinations are widely used in practice.

Similarly, 4-dimethylamino-4′-isopropyl benzophenone functions as a photoinitiator [104].

Amines can act as reductants for excited states of other electron acceptors, too. Again, two possibilities exist: (1) amine and acceptor form a CT; (2) the complex formation takes place either with the excited state of the amine or with that of the electron acceptor (see discussions of ketone-amine combinations). Examples for the former principle are such combinations as: DMA-nitrobenzene [105], triphenylamine-tetracyano ethylene, 4-nitrophenole, 4-aminochlorobenzene [106], tributylamine-tetrachloromethane [107], DMA-substituted chloroacetic acids [108, 109].

So far, detailed information on the photochemistry of these combinations is not available. It can be expected that similar reaction pathways hold as given in Scheme 3. In some cases, end-group analyses of polymers prepared clearly indicate that initiation of polymerization takes place by radicals derived from both partners. The radical mechanism is also decided through the inhibitory effect of air or benzoquinone. For some combinations, the kinetic non-ideality with respect to the low initiator exponent ($\beta < 0.5$) can be interpreted on the basis of significant initiator dependent termination, particularly by degradative initiator transfer mechanism.

Also, the PET between polynuclear aromatic hydrocarbons (naphthalene, anthracene, phenanthrene, perylene) or heteroaromatics (phenazine, acridine) as acceptors and amines as donors can be used for polymerization initiation of AN and alkyl methacrylates [111–113]. In general, a reaction course as outlined in Scheme 3 also acts with these combinations.

The R_p values for butyl methacrylate polymerization using DMA increased by 1–1.5 orders of magnitude on going from benzene to acetonitrile solution. The type of solvent also strongly influences the exponents of the general kinetic expression (9) of these systems; see Table 4. Whereas the exponents for the light intensity absorbed and the acceptor concentration remain constant, a remarkable solvent influence exists on monomer and donor exponents. For an explanation, it is assumed that solvate separated radical ions were formed in the polar acetonitrile from photodissociation of exciplexes of the acceptors with DMA. These radical ions were apparently the primary active products generating the polymerization chain. In benzene, initiation occurred by a free radical mechanism. But contrary to Scheme 3, the formation of ternary excited complexes both in the triplet-state and singlet-state with monomers also has to be taken into account. The quenching constants for the anthracene-DMA exciplex with butyl methacrylate are 9×10^5 mol l^{-1} s^{-1} (in benzene) and 10^8 mol l^{-1} s^{-1} (in acetonitrile).

$$R_p = [M]^\alpha I^\beta_{abs}[A]^\gamma [D]^\delta \qquad (9)$$

Further examples for a PET involving amines are: quinoline-dibenzoyl peroxide [114], rhodamine 6G-dibenzoyl peroxide [115], and auramine *O*-dibenzoyl peroxide [116] systems. The use of coloured amines makes it possible to initiate the polymerization with visible light, which is favorable for several practical applications. Again, the photopolymerization process proceeds by a free radical mechanism, and therefore, dye moieties are incorporated as endgroups into the polymer molecules.

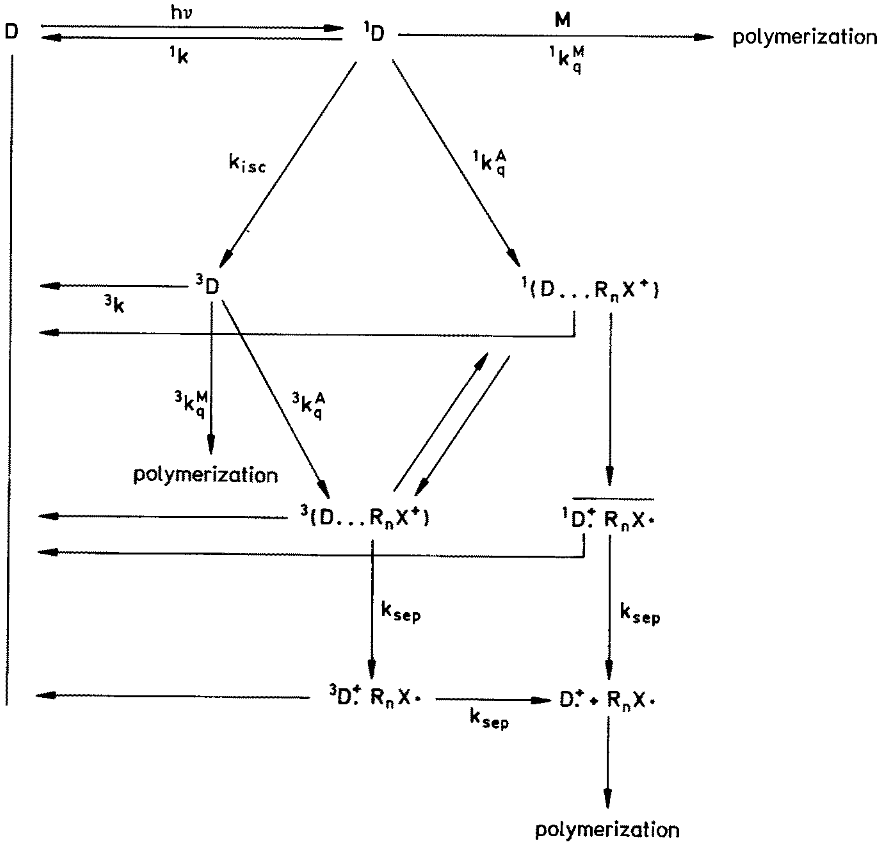
Also, the PET between excited states of donors and various onium compounds yields radicals [11, 52, 117–123]. However, the mechanism in the presence of monomers is very complicated due to the interaction possible between excited species and monomers; see Scheme 9. So far, many details of that scheme are unsolved or not strongly supported by experimental data.

Table 4. Solvent influence on the kinetics of butyl methacrylate (BMA) photopolymerization with *N*,*N*-dimethylaniline and various acceptors [112] (λ = 366 nm, 288 K)

Acceptor	Exponents of kinetic expression (9)							
	in benzene				in acetonitrile			
	α	β	γ	δ	α	β	γ	δ
Phenazine	1.02	0.50	0.51	0.07	2.00	0.55	0.50	0.26
Acridine	1.08	0.50	0.52	0.13	2.10	0.57	0.50	0.37
Anthracene	1.00	0.46	0.54	0.08	2.00	0.54	0.52	0.48

Such compounds as: polynuclear aromatics, heteroaromatics, ketones, quinones and dyes can serve as donors. Both excited singlet and triplet-states of these products can be involved in the PET. Diaryliodonium salts, triarylsulfonium salts, phosphonium salts, ammonium salts, pyrylium and thiapyrylium salts possess enough thermal stability and corresponding reduction potential to function as electron acceptors (R_nX^+). In order to select suitable photoinitiator systems based on compounds discussed, the Weller-Eq. (5) can be employed.

The application of those systems as photoinitiators depends on some fundamental conditions: (1) The reaction pathways involving onium salts must proceed faster than the monomolecular deactivation, the bimolecular quenching with monomers (data for triplet quenching in ketone-MMA systems see Table 3) and with oxygen, respectively; (2) Because an efficient polymerization initiation normally needs uncorrelated radicals, the efficiency of formation of free D^{+} and $R_nX\cdot$ must be high (≥ 0.5). Therefore, all reactions leading to ground-state molecule should be depressed; (3) The fragmentation of $R_nX\cdot$ must occur with high rate constants to compete efficiently with the back electron transfer outside or inside of a cage.



Scheme 9

But, there are some hints that exciplexes between the donors and acceptors discussed can be quenched by monomers, too. Then, that processes lead to a less efficient polymerization reaction [52].

As can be seen in Table 5, if the thermodynamic prerequisites are obeyed (e.g. $\Delta G_{et} \ll 0$), the quenching constants of the singlet-states of various systems, measured by life-time experiments, are nearly diffusion controlled. Evidence in support of the PET mechanism has been obtained by the detection of $D^{\ddagger}$ species of some donors using their typical spectral data. Additionally, the isolation of the expected fragmentation products of the $R_nX\cdot$ points to this mechanism; see Eq. (10).

$$R_nX\cdot \rightarrow R_{n-1}X + R\cdot \tag{10}$$

$$R_{n-1}X = ArI,\ Ar_2S,\ R_3P,\ R_3N$$

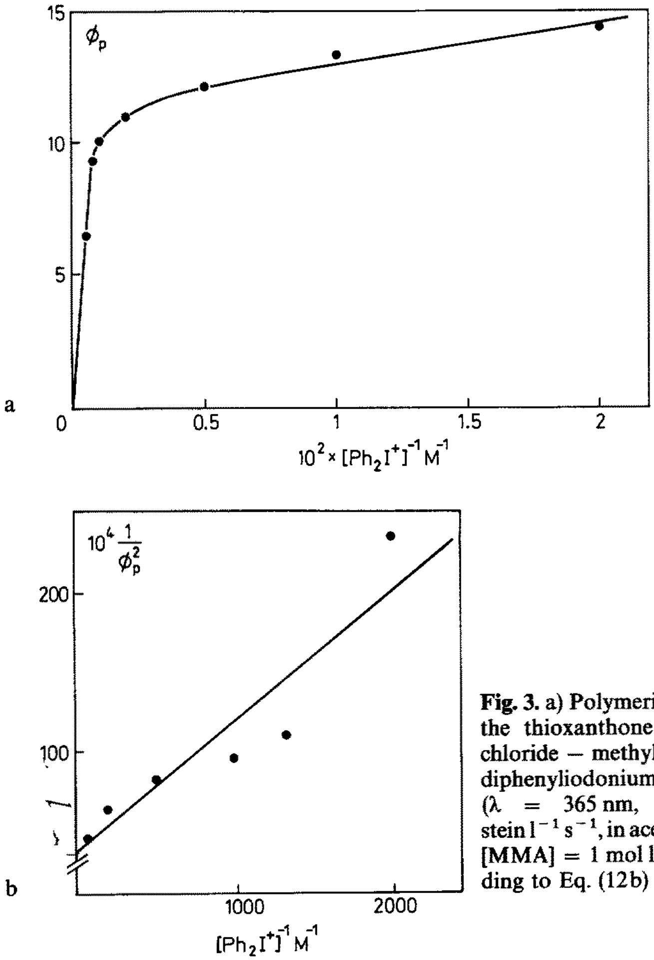


Fig. 3. a) Polymerization quantum yield of the thioxanthone – diphenyliodoniumchloride – methyl methacrylate system vs. diphenyliodoniumchloride concentration (λ = 365 nm, I_{abs} = 5×10^{-7} einstein $l^{-1} s^{-1}$, in acetonitrile/water 90 vol%, [MMA] = 1 mol l^{-1}); b) Plot corresponding to Eq. (12b)

Since various $D-R_nX^+$ combinations exhibit a high value of ${}^1k_q^A$, at concentrations of onium salts $\geqq 5 \times 10^{-2}$ mol l^{-1} competitive bimolecular quenching reactions of the singlet-state are suppressed, but the isc-process is still possible. The efficiencies of isc (η_{isc}) in the presence of R_nX^+ and monomers calculated by Eq. (11) are outlined in Table 5. In contrast to the singlet-state reaction, most constants of the triplet quenching by R_nX^+ are only in the order of 10^7 mol l^{-1}. That is surprising, because the calculated ΔG_{et}^3 values predict diffusion controlled reactions in these cases. Again, direct evidence for the PET has been obtained from laser photolysis studies, CIDNP measurements, as well as from the isolation corresponding reaction products.

$$\eta_{isc} = k_{isc}/{}^1k_q^A[R_nX^+] + {}^1k + k_{isc} + {}^1k_q^M[M] \qquad (11)$$

As expected, the quantum yields of the onium salt decomposition or of the donor decrease (ϕ_{in}) depend on the R_nX^+ concentration. Assuming, that only one excited state is involved in the PET, a correlation corresponding to Eq. (12) can be deduced. Indeed, the experimental data obey this relationship (see Fig. 3). Values for ϕ_{in} measured under identical experimental conditions are listed in Table 5. Using the slope and intercept of the linear plot corresponding to Eq. (12a), some constants or constant ratios of the kinetic Scheme 9 can be calculated.

$$\frac{1}{\phi_{in}} = \frac{k_{sep} + k_{-e}}{{}^*k_q^A{}^*\tau_0 k_{sep}} \frac{1}{[R_nX^+]} + \frac{k_{sep} + {}^*k_q^A}{k_{sep}} \qquad (12a)$$

$$\frac{1}{\phi_p^2} \approx \frac{1}{\phi_{in}} \qquad (12b)$$

${}^*\tau_0$ = life time of the excited state in absence of R_nX^+

The aforementioned systems are able to start both radical and cationic polymerization processes (see also Sect. 4.2).

Some quantum yields of radical polymerization (ϕ_p^r; for definition see Eq. (2b)) with the model monomer MMA are presented in Table 5. It is obvious that a variety of parameters acts on this value. Mainly, the participation of initiator molecules and of primary radicals on chain termination are responsible for the differences in the ϕ_p-values.

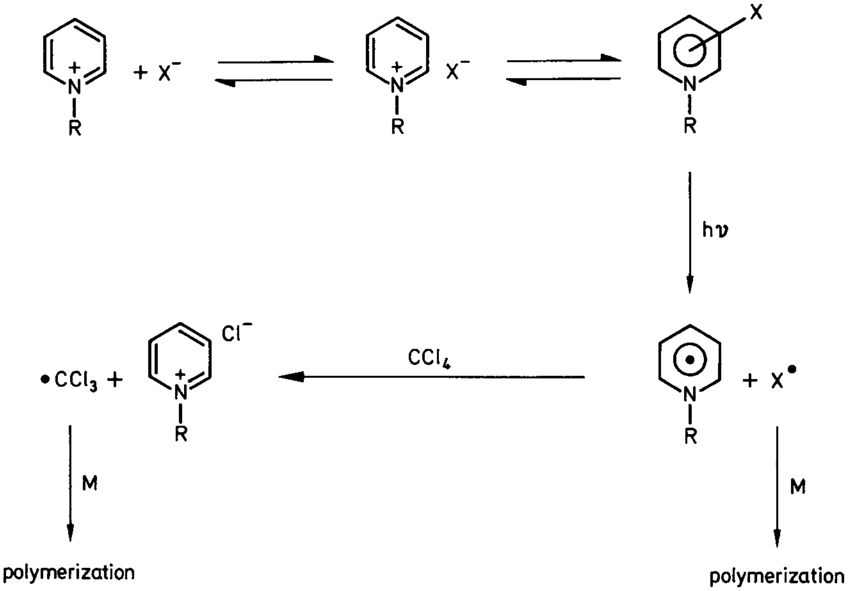
In principle, the photoreactions of CT's are able to offer a great number of photoinitiator systems for radical polymerization. But, so far, this subject has only received little attention, and the current knowledge relative to the photochemistry of such complexes is poor. In addition to the amine complexes mentioned above, chinoline-bromine [124–127], chinoline-chlorine [128], 2-methylpyridine-chlorine [129], pyridine-bromine [130], *N*-vinylpyrrolidone-bromine [131], acridone-bromine [132], acridone-chlorine [133], benzophenone-SO_2 [134], isoquinoline-SO_2 [135, 136], and 2-methylquinoline-SO_2 [136] combinations are used for radical polymerization of AN, alkyl methacrylates, acrylic and methacrylic acid, and for

Table 5. Free reaction enthalpies (ΔG_{et}), rate constants for electron transfer between excited singlet (${}^1k_q^A$) and triplet state (${}^3k_q^A$) of donor and onium salts, efficiencies of isc-process of the donor in presence of onium salts (η_{isc}), quantum yields of onium salt decomposition (ϕ_{in}) and of polymerization (ϕ_p^r) of methyl methacrylate (measured in acetonitrile/water 90 vol%)

Donor	Onium salt	ΔG_{et}^1 (eV mol^{-1})	${}^1k_q^A \times 10^{-9}$ (l mol^{-1} s^{-1})	ΔG_{et}^3 (eV mol^{-1})	${}^3k_q^A \times 10^{-7}$ (l mol^{-1} s^{-1})	η_{isc} [a]	ϕ_{in} [a,b]	ϕ_p^r [a–c]
Anthracene	Ph_2I^+	−1.7	16	−0.6	0.7	0.47	0.22	36
	Ph_3S^+	−0.8	15	0.4	<0.01	0.51	0.20	41
	$(NCCH_2)Ph_3P^+$	−1.5	17			0.54	0.40	93
	Ph_4P^+	−0.9	7				0.15	53
9.10-Diphenylanthracene	Ph_2I^+	−0.8	18				0.21	38
	Ph_3S^+	−0.3	11				0.27	42
	$(NCCH_2)Ph_3P^+$	−0.3	9				0.24	46
2.4.5-Triphenyloxazole	Ph_2I^+		4.5				0.03[d]	26
	Ph_3S^+		2.8				<0.01[d]	42
Benzophenone	Ph_2I^+	−0.2		~0	2.0	1	0.06	20
Thioxanthone	Ph_2I^+	−0.8	4.8	−0.5	200	0.90	0.27	43
10-Methylacridone	Ph_2I^+	−0.8	9.6	−0.5	350	0.18	0.13	60
Thiopyronine	Ph_2I^+	−0.6	18	−0.3	1			
Fluoresceine	Ph_2I^+	−0.7	19	−0.2			0.55	

[a] Concentration of donor and onium salt 1×10^{-2} mol l^{-1}; [b] $\lambda = 365$ nm, absence of oxygen; [c] Incident light intensity $4.7–5.1 \times 10^{-7}$ einstein min^{-1}; concentration of methyl methacrylate 3.8 mol l^{-1}; [d] $\lambda = 313$ nm

graft copolymerization onto wool or Nylon 6. However, whether the PET mechanism is involved is not certain in each case. In halogen complexes, a homolytic photodissociation reaction could also occur. Interestingly, the exposure of halogen complexes in AN solution gives high-molar-weight polymers with ordered structures and improved properties. But in general, those systems possess only a small dark stability due to the partial electron transfer in the complex molecule.

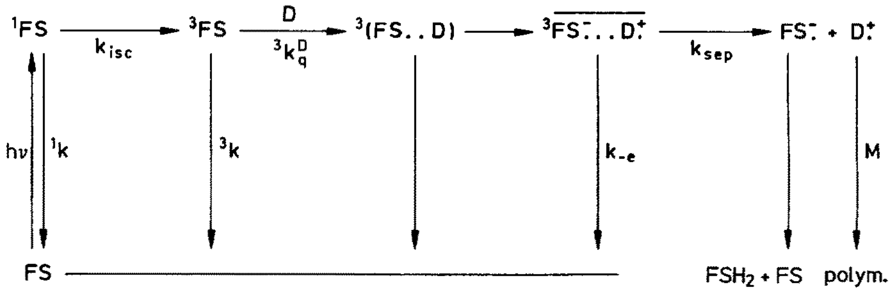


Scheme 10

A PET in intramolecular CT's between pyridinium ions and bromide, chloride or thiocyanate ions for polymerization initiation is described, too [137–139]. As expected, an equilibrium exists among free ions, ion pairs, and CT, which is shifted to the free ions in polar solvents and to the complex in a less polar solvent. That complex serves as the photosensitive species for the polymerization (see Scheme 10). The photodecomposition of the CT yields radicals of the former anion and *N*-alkylpyridinyl radicals. Probably, the photopolymerization is initiated only by X· radicals, whereas latter radicals terminate the chain reaction. By addition of tetrachloromethane, the polymerization rate is increased owing to an electron transfer between the nucleophilic pyridinyl radical and CCl_4 (indirect PET). As a result, the terminating radicals are scavenged and electrophilic $\cdot CCl_3$ radicals are produced.

Polymerization initiating species can be generated from dyes (FS) through PET [140, 141]. Two possibilities exist: (1) dye-reduction reactions (D-R or D-D mechanism; see Scheme 11); (2) dye-oxidation reactions.

Due to the extremly delocalized nature of the $\pi\pi^*$ transition state, dyes containing quinoide chromophores are favored for a reduction pathway. The experimental evidence for PET results from identification of the corresponding intermediates (dye-triplet, semiquinone radicals, donor radicals) by means of flash photolysis, CIDNP, and ESR experiments, respectively [142]. Photoreducable dyes are: diphenyl- or azadiphenyl methane, xanthene and triphenylmethane dyes, porphyrines and phthalocyanines. As electron donors are used: amines, compounds with α-CH bonds to carbonyl or carboxyl groups [143], ascorbic acid [144], sulfinic acid and its derivatives, substituted thioureas. All these donors very quickly transfer a proton from their cation radical to the semiquinone anion radical, necessary to get high quantum yields of initiating species.



Scheme 11

Furthermore, an intramolecular PET in ion-pairs involving dye cations is possible. So, cyanine borates exist in ester solution as ion pairs [145]. The irradiation of that species initially creates cyanine radicals and alkylboranyl radicals. Latter species fragment to triphenylborane and alkyl radicals; see Eq. (13). In support of the assumption of an intra-ion-pair electron transfer, no cyanine radicals have been obtained by irradiation in acetonitrile solution.

$$(Cy)^+(n\text{-}C_4H_9BPh_3)^- \xrightarrow[532\,\mathrm{nm}]{h\nu} Cy\cdot + n\text{-}C_4H_9\dot{B}Ph_3 \rightarrow Ph_3B + n\text{-}C_4H_9^{\cdot} \qquad (13)$$

$$^3FS + O_2 \rightarrow FS^{+\cdot} + O_2^{-\cdot} \qquad (14a)$$

$$^3FS + R_nX^+ \rightarrow FS^{+\cdot} + R\cdot + R_{n-1}X \qquad (14b)$$

The triplet-state of dyes can interact in different ways with oxygen. Among these, a PET yields radicals, which are able to initiate polymerization; see Eq. (14a). The photooxidation of dyes can also be effected by onium salts [146–148]. The general mechanism of this process is similar to that outlined in Scheme 11, taking into account that ^3FS is the donor; see Eq. (14b). However, with strong electron acceptors, such as arenediazonium salts, the singlet-state reacts, too. Again, the radical of the former onium ion fragments; see also Eq. (10). In the presence of a reducing agent (supporting donor), the situation is more complicated, because dye reduction can also occur; see Eq. (15). Based on the concentration ratios this mechanism competes with the normal oxidation process.

$$^{1,3}FS + D \rightarrow FS^{\cdot -} + D^{\cdot +} \tag{15a}$$

$$FS^{\cdot -} + R_nX^+ \rightarrow FS + R_{n-1}X + R\cdot \tag{15b}$$

On the basis of the PET of dye systems, water-soluble photoinitiators can be created, for which many application fields exist.

Also, coordination compounds and metal carbonyls are able to undergo a PET, resulting in initiating radicals [63]. Recently investigated examples are: iron chloride based ammonium salts [149], vanadium(V) organo-metallic complexes [150], and metal sulfoxide complexes [151]. However, the polymerization efficiency of some systems is only low due to redox reactions between the central metal ion and the growing polymer radical, and the low quantum yields of PET.

$$X \xrightarrow{h\nu} R_{nu}\cdot \xrightarrow[k_e]{R_nX^+} R_{nu}^+ + R\cdot + R_{n-1}X \tag{16a}$$

$$X \xrightarrow{h\nu} R_{nu}\cdot \xrightarrow[k_e]{RY} R_{nu}^+ + R\cdot + Y^- \tag{16b}$$

Some radical photoinitiator systems are based on an indirect PET [11]. The fundamental principle is given in Eq. (16). After photoreaction, a nucleophilic

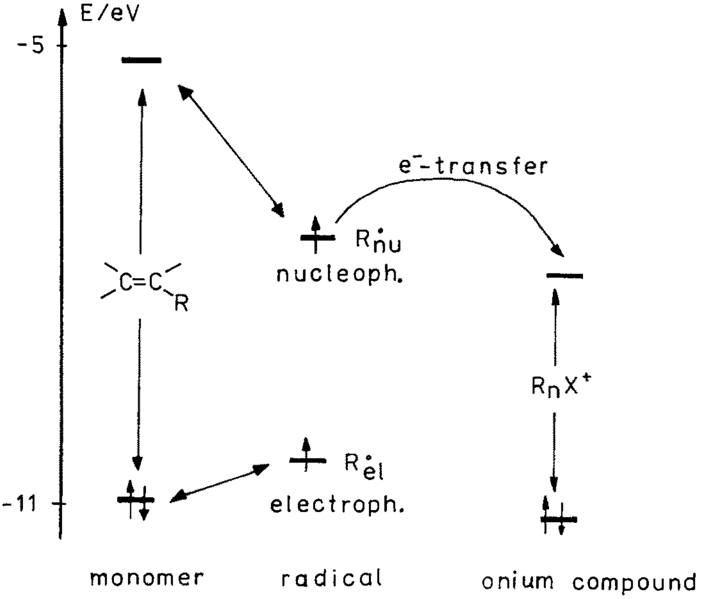


Fig. 4. FMO scheme for the indirect photoinduced electron transfer between nucleophilic radicals and onium salts in presence of monomers

radical is formed, which usually is not capable of varrying out radical polymerization (see Fig. 4). But, $R_{nu^{\cdot}}$ radicals may reduce onium salts or organic halogen compounds in a dark reaction, if the thermodynamic conditions are favored for electron transfer.

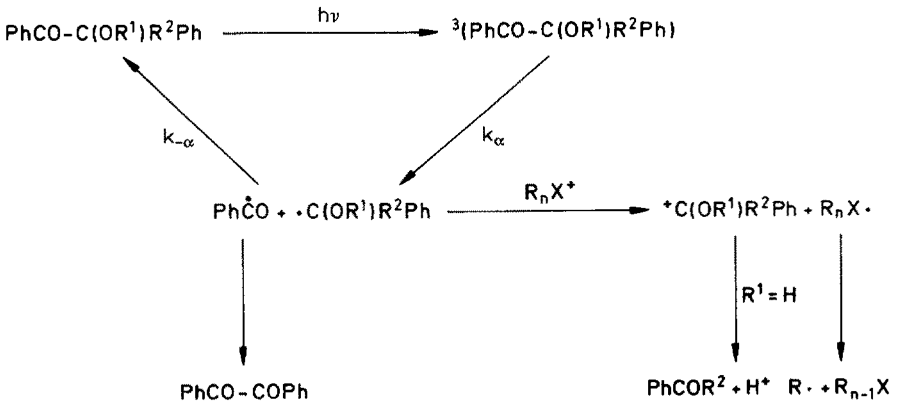
The following photoreactions can be used for $R_{nu^{\cdot}}$ formation:

- α-cleavage of benzoin derivatives, benzil ketals, 2-alkoxyacetophenones and related compounds [122, 152–156],
- hydrogen abstraction reactions of ketones and quinones [120–122, 157],
- decay of exciplexes of benzophenones and amino substituted aromatic ketones (e.g. MK, Ac, MAc),
- redox reactions of coordination compounds (e.g. formation of $CO_2^{-}\cdot$) [158–160].

Key features for the reaction of such systems are: (1) The photochemical formation of $R_{\dot{n}u}$ must be initiated with light of wavelengths out of the spectral response of onium salts and halogen compounds, to prevent inner filter effects; (2) The photoreaction forming $R_{\dot{n}u}$ should proceed very efficiently; (3) Compared to other reactions of $R_{\dot{n}u}$, the electron transfer between $R_{\dot{n}u}$ and R_nX^+ or RY must be favored thermodynamically and kinetically.

The k_e-values for the reaction between onium salts and $R_{\dot{n}u}$ are related to the electron acceptability of R_nX^+ (e.g. diphenylketyl radical: $3 \times 10^8\ l\ mol^{-1}\ s^{-1}$ for Ph_2I^+; $1 \times 10^5\ l\ mol^{-1}\ s^{-1}$ for Ph_3S^+). From these data it can be deduced that with iodonium salts, fast electron transfer occurs even if their concentration is in the order of $10^{-2}\ mol\ l^{-1}$. With halogen compounds it was found that chlorine or bromine-containing compounds (e.g. mono- or polyhalogen alkanes, benzylhalogenides, α- or β-substituted esters) exhibit the best acceptor properties, whereas C—F bonds in analogous fluorine-containing compounds react only very inefficiently [161].

The reactions of benzoin ether-onium salt systems are illustrated in Scheme 12. All expected products have been found. The quantitative formation of diketones also in presence of onium salts indicates that the electrophilic benzoyl radical does not efficiently react with R_nX^+. In consequence of the recombination of acyl and



Scheme 12

ether radical ($k_{-\alpha}$), CIDNP signals of the initial benzoin ethers were found. In presence of R_nX^+ the intensity of signals may approach zero. Both acyl and ether radicals formed by the α-cleavage of the benzoin derivatives were detected by means of ESR spin trapping with benzylidene-*tert*-butylamine *N*-oxide in the absence of onium salts. In their presence only the signals of acyl radicals and $R\cdot$ were found.

The quantum yields of onium salt decomposition (ϕ_{in}) give important hints of the effectivity of such systems for polymerization initiation. For some combinations the ϕ_{in} are listed in Table 6. Various systems exist, in which almost all photochemically formed $R_{\dot{n}u}$ were consumed by the R_nX^+; see the small differences in ϕ_α and ϕ_{in}. Data of the action of these photoinitiator systems in radical polymerization of MMA are given in Table 6. In order to discuss the dependence of the ϕ_{in}-values it must be kept in mind that acyl radicals, produced simultaneously with $R_{\dot{n}u}$ (see Scheme 12), also initiate the polymerization chain. But, as can be seen by the ratio of polymerization rates in presence (R_p) and in absence of onium salts (R_p^0), the decomposition of R_nX^+ by $R_{\dot{n}u}$ increases the ϕ_p^r-values.

Table 6. Photoinduced decomposition of onium salts by $PhCO{-}C(OR^1)R^2Ph$: quantum yields of α-cleavage (ϕ_α), quantum yields on onium salt decomposition (ϕ_{in}), quantum yields of polymerization of methyl methacrylate (ϕ_p^r) and the ratio of polymerization rate in presence (R_p) and absence of onium salts (R_p^0) (measured in acetonitrile/water 90 vol%, $\lambda = 365$ nm, absence of oxygen, concentration of onium salt 1×10^{-2} mol l^{-1})

R^1	R^2	ϕ_α [a]	R_nX^+	ϕ_{in}	ϕ_p^r	R_p/R_p^0 [b]
$(CH_3)_2CH$	H	0.39	Ph_2I^+	0.12	53	1.2
			Ph_3S^+	0.019		
CH_3CO	H	0.33	Ph_2I^+	0.044	30	1.6
			Ph_3S^+	0.037	22	1.2
H	Ph	0.10	Ph_2I^+	0.032	26	1.9
			Ph_3S^+	0.016	14	1.0
CH_3	OCH_3	0.50	Ph_2I^+	0.22	60	1.0
			Ph_3S^+	0.18		

[a] Measured in presence of oxygen; [b] Concentration of MMA 3.8 mol l^{-1}, absorbed light intensity 3.1×10^{-7} einstein min^{-1}

4.2 Cationic Polymerization

As outlined in Scheme 2, for cationic photopolymerization a photoinduced formation of species X^+ or Lewis acids is required [162]. Such species are formed both by PET between neutral donors and acceptors (see Scheme 3), between neutral donors and positive charged acceptors (see Schemes 9 and 11), respectively, and by an indirect PET between nucleophilic radicals and onium salts or halogen compounds (see Eq. (16) and Scheme 12). Therefore, combinations of compounds, whose light-induced reactions are based on the pathways given above, are usable as photoinitiators for cationic polymerizations, too. Prerequisites for the use of cations as electron acceptors are their inability to initiate thermal polymerization reaction at room temperature and their thermal stability. The above mentioned onium salts possess these properties [163, 164].

In general, the fundamental statements given above for the photochemistry in these combinations can be extended to the subject discussed in this section. But, so far, only a little information exists on the influence of monomers on the overall processes.

So far, only a few examples of cationic photopolymerizations using PET corresponding to Scheme 3 have been described [10, 13, 165]. In the ternary system cyclohexene oxide, 9.10-dicyano anthracene and polynuclear aromatics, the polymerization of the former is initiated by the radical cations of the aromatic hydrocarbons formed via the PET with the dicyano compound.

More results are available for the PET between neutral donors and onium salts. Such compounds as polynuclear aromatics [166–170], ketones [168–171], heteroaromatics [172], and dyes [166] can be used as electron donors for that purpose. Because they have lower oxidation potentials ($E^{ox}_{1/2} \approx 0.5$ V) diaryliodonium salts are better as suitable acceptors for a PET than triaryl sulfonium salts ($E^{ox}_{1/2} \approx 1.2$ V). Phosphonium and ammonium salts are not useful electron acceptors in photoinitiator systems for cationic polymerization. Their decomposition results in nucleophilic compounds (Nu; see Eq. (10), $R_{n-1}X = R_3N$ or R_3P), which terminate the chain reaction of the cationic polymerization; see Scheme 2. The initiator of cationic polymerization is derived from the light-absorbing donor, in contrast to the situation with the direct photolysis of onium salts. Because most of the described experiments have been run under conventional laboratory dry conditions, initiation by these primary formed cation radicals takes place in competition with their reactions with small amounts of protogenic and non-protogenic impurities present. Under these circumstances, the dominant initiating species appears to be a Brønsted acid. It is likely that even under rigorously dry polymerization conditions, a number of initiating species including cations, cation radicals and Brønsted acids may be involved. But in all cases, only onium salts bearing low- or non-nucleophilic anions X^- (e.g., PF_6^-, AsF_6^-, SbF_6^-) are suitable, due to the fast termination reactions with other anions; see Scheme 2.

Table 7. Quantum yields (ϕ_p^c) and rates (R_p) of the polymerization of 2.3-epoxypropyl phenyl ether with diphenyliodoniumhexafluorophosphate coinitiator systems (measured in bulk, $\lambda = 365$ nm, absorbed light intensity 2.8×10^{-6} einstein min^{-1})

Light absorbing component	ϕ_p^c	$R_p(N_2)/R_p(O_2)$
Anthracene[a]	53	1.13
9.10-Phenanthrenequinone[a]	55	1.17
Benzophenone[b]	21	0.99
Benzoin isopropyl ether[a]	42	0.70
2-Phenylbenzoin[c]	30	0.71
Benzil dimethylketal[a]	170	

[a] Concentration of $Ph_2I^+PF_6^-$ 2×10^{-2} mol l^{-1}; [b] Concentration of $Ph_2I^+PF_6^-$ 5×10^{-2} mol l^{-1}; [c] Concentration of $Ph_2I^+PF_6^-$ 4×10^{-2} mol l^{-1}

Table 7 give some data of the polymerization quantum yields (ϕ_p^c) as a measure for the efficiency of various donor-diphenyliodonium salt combinations in the cationic polymerization of PGE.

Carbocations generated via indirect PET of carbon-centered free radicals with onium salts according to reaction (16a) have been utilized to initiate cationic polymerization of monomers such as alkyl vinyl ethers, cyclic ethers and epoxies [173–175]. Again, benzoin derivatives, benzil ketals, and special substituted azo compounds act as free radical promoters; see Scheme 12. Also, electrophilic radicals photochemically generated can contribute indirectly to the formation of carbocations as shown in Eq. (17). Radicals $R^{1\cdot}$ or $R^{2\cdot}$ formed by photo-cleavage of the initial compound R^1-R^2 can react according to reaction (18). Cyclic ethers (e.g. epoxides, THF) function as hydrogen donors and vinyl compounds bearing donor substituents R^3 (e.g. alkyl vinyl ethers) serve as sources for the addition reaction (18b). The carbon-centered radicals thus formed are capable of reducing diaryliodonium and triarylsulfonium ions according to reaction (16a). Examples for such combinations are: aroyldiarylphosphine oxides-alkyl vinyl ethers or THF [176, 177], triphenylsulfonium hexafluorophosphate-glycidyl ethers or THF [178–180]. Evidence in support of the pathways discussed are given by laser photolysis experiments, the incorporation of R^1 moieties into the polymer formed (e.g. incorporation of phosphorus by the phosphine oxides) and ϕ_p^c values $\gg 1$.

$$R^1-R^2 \xrightarrow{h\nu} R^{1\cdot} + R^{2\cdot} \tag{17}$$

$$R^{1\cdot} + H-\overset{|}{\underset{|}{C}}- \rightarrow R^1-H + \cdot\overset{|}{\underset{|}{C}}- \tag{18a}$$

$$R^{1\cdot} + CH_2=CH-R^3 \rightarrow R^1CH_2-\dot{C}H-R^3 \tag{18b}$$

Presumably, a PET is involved also in the cationic photopolymerization of epoxides with metal arene complexes [181, 182].

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Electron Transfer Processes in Imaging

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Table of Contents

Many photoimaging technologies involve electron-transfer processes in the critical image capture, or light-sensitive, step of the process. This chapter reviews the photochemical and photophysical basis for these processes. The chapter is divided into several major sections: an introduction to basic imaging concepts; a brief discussion of the chemistries and photochemistries involved in conventional silver halide based imaging processes and those involving other semiconductors as primary light absorbers; and sections describing less conventional processes that are based on organic photochemical charge transfer processes (electrophotography, color formation systems, and photopolymerization processes).

Topics in Current Chemistry, Vol. 156

David F. Eaton

1 Introduction

Electron-transfer processes are ubiquitous in photochemistry [1]. Fundamentally, this is because electronically excited states are both better oxidants as well as better reductants than their parent ground states. This reactivity arises from depopulation of the highest occupied molecular orbital (HOMO) of the molecule on excitation and promotion of an electron to the lowest unoccupied MO (LUMO). The new electronic configuration processes an unpaired electron with high reducing potential in one orbital (LUMO) and a hole of high oxidizing potential in another (HOMO). Much of the photochemical reactivity of organic, inorganic, and organometallic species can be rationalized by considering the characteristic reactions anticipated from this photogenerated electron/hole pair within the molecule and its interactions with other molecules which might be nearby.

Examples of well-known photochemical reactions which involve electron transfer include the primary step in plant and bacterial photosynthesis [2], the photoreduction of ketones by amines [3], a series of sensitized isomerizations of olefins and small ring compounds such as cyclopropanes or of strained polycyclics such as quadricyclane to norbornadiene or Dewar benzenes to benzenes [4], and the reactions of electron-rich substrates in the presence of oxygen which proceed via superoxide [5]. These reactions and others have proved valuable for synthetic applications in addition to their fundamental interest to photochemists.

Photoimaging is a methodology for the capture and replication of information which uses photons. The technology of photoimaging has spawned several large industries which impact our daily lives in major ways. Conventional (silver halide based) photography, electrophotographic office copying, graphic arts processes such as printing and reprography, and the newer techniques of electronic imaging are examples. In addition, there are a host of "unconventional" imaging processes that are less familiar but equally vital to our modern way of life. These latter processes are used to produce printed circuit boards, integrated circuits, and holographic optical elements, among a myriad others. Many of these imaging technologies, conventional and unconventional, involve electron transfer processes in the critical image capture, or light-sensitive, step of the process. This chapter reviews the photochemical and photophysical basis for these processes.

The chapter is divided into several major sections: an introduction to basic imaging concepts; a brief discussion of the chemistries and photochemistries involved in conventional silver halide based imaging processes; and sections describing less conventional processes that are based on organic photochemical charge transfer processes (electrophotography, color formation systems, and photopolymerization processes). The emphasis will be on the elementary electron transfer processes involved in the technologies. Details of the imaging processes, beyond the introductory level, are not considered. Several monographs may be consulted [6].

2 Photoimaging Processes

All photoimaging processes can be reduced to three elementary steps: image capture, image rendition, and image readout (Fig. 1). The overall properties of the imaging system will depend on all three stages, though the nature of the readout scheme used is often a function of the physical changes in the medium which are effected by the initial two stages. We are most familiar with imaging systems which provide a visual readout image, that is one which can be detected by our eyes. Many systems exist which require alternate mechanisms for readout.

The fundamental photochemistry of the imaging system resides in the image capture step. A final photoimage will result only if the light-struck regions of the sensitive medium can be differentiated from the unexposed regions, either immediately after exposure of the medium to light, or at some later time, by some physical process. Conventional silver halide photography (black and white) relies on the opacity of the developed silver image to visually contrast with the unexposed background, which may be white if the image is printed on photographic paper, of clear if it is on a transparent film base. In color photography, the contrast is also provided by differential light absorption or transmission, but now with spectral selectivity across the visible region as provided by discrimination of the dyes produced. In electrophotography, visual contrast is provided in the electrostatic toning step, attracting (usually) black toner particles to regions of the active

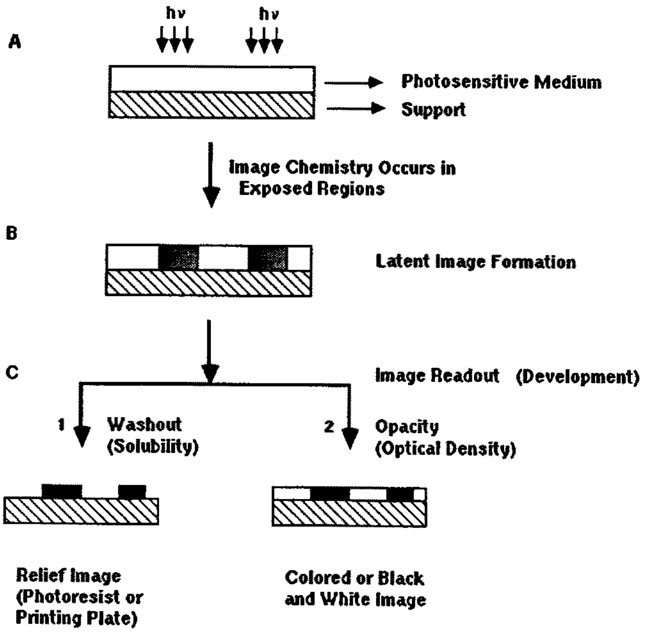


Fig. 1. Elementary steps of imaging processes: *A* Image capture; *B* image rendition (latent image formation); *C* image readout (development)

medium which retain their dielectric character after exposure. Both silver halide photography and electrostatic imaging can each provide a black and white visual contrast image to be discerned by the eye, but the fundamental image differentiation processes are much different in the two processes. Similarly, unconventional imaging processes can be initiated by different image capture chemistries, but can also provide visual readout images, or they can provide very unusual kinds of readout. One such unconventional process is photopolymerization. Another is photocrosslinking. Photopolymerization is the generic process of converting smaller molecules into larger ones triggered by light, that is the photochemically activated conversion of monomers into high polymers. Photocrosslinking creates one or more new covalent bonds between preexisting units; photodimerization is a specific type of photocrosslinking. Photocrosslinking doubles the molecular weight of the product for each new linkage created, while photopolymerization gives conversion to high molecular weight which depends directly on the degree of polymerization. Photopolymerization can be either free radical or ionic in nature, though most imaging processes involve vinyl free radical addition polymerization reactions. Photocrosslinking chemistry can employ any prototypal small molecule photochemistry which creates a covalent bond.

Both photopolymerization and photocrosslinking processes can be used to produce images of various kinds. Electron transfer photochemistries can be involved in the image capture step for both. Examples of the kind of images that can be produced by these techniques are three-dimensional relief (where differential solubility of the imaged and unimaged areas provides the physical basis for readout through solvent treatment) to produce printing plates or photoresist structures, light scattering images that can be viewed in projection (image differentiated by phase separation or index of refraction modulation), colored or black-and-white contrast images (where pigment toning is used to develop an image differentiated through tackiness of the image surface), or images that can be wetted by inks and differentiated from an ink-repellant background to produce lithographic printing media. Figure 2 illustrates some of these techniques. Many other methods have been developed.

Other photochemistries than photopolymerization or photocrosslinking have been used in unconventional imaging systems, for example diazide resists (photo-

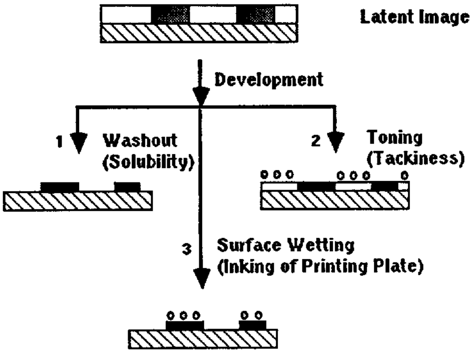


Fig. 2. Illustration of several unconventional imaging processes: *1* Photoresist formation by washout development; *2* pigment toning of sticky (tacky) unexposed photopolymer; *3* inking of a printing plate surface

Wolf reaction) and *o*-nitrophenylaldehyde photochemistry, but they do not involve electron transfer processes, and so are excluded from this chapter. Similarly, radiation or electron-beam initiated imaging chemistries are excluded.

Several other simple photochemistries can be used to produce images. Photo-oxidation of leuco dyes can be used to form colored images. Photoreduction processes, e.g., of metal ions to produce metallic image regions, can also be used. These photochemistries will be described also.

Finally, dyes may be used in several imaging processes to extend the inherent spectral sensitivity of an imaging process to longer wavelengths, especially to visible or near infrared regions of the spectrum. These sensitization processes are industrially very important to provide panchromatic sensitivity or sensitivity to special light sources such as lasers. This review will describe those spectral sensitization processes which involve electron transfer, but will ignore those processes based on more conventional mechanisms.

3 Silver Halide Systems

Silver halide systems are the dominant medium for rapid white light image capture. The fundamental photochemistry is deceptively simple; the technology involved in industrial implementation of the chemistry is prodigious.

Silver halide crystals are wide band gap semiconductors. Photographic emulsions are complex formulations, but they consist essentially of a suspension of silver

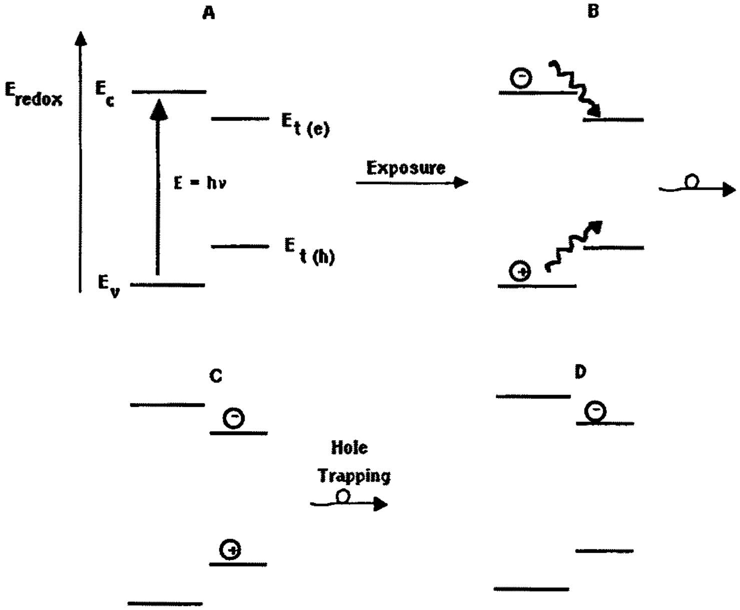


Fig. 3. Energy levels in AgX. E_v = valence band; E_c = conduction band. Exposure process: *A* light absorption; *B* charge motion to traps; *C* trapped charges; *D* latent image

halide microcrystals in polymeric binders, especially gelatin. Absorption of a photon by intrinsic silver halide materials produces an electron/hole pair, which separates in the crystal, eventually to recombine or to be trapped either at defect sites or at chemical traps added deliberately to the material (Fig. 3). Trapped charges are only slowly detrapped, and form the latent image upon which the success of silver photography is based.

Immersion of the exposed silver halide film in a developer transforms the latent image areas into metallic silver, visible as dark, absorptive regions in black and white films. The function of the developer is to supply electrons to the developing silver halide microcrystal; this is acomplished using hydroquinone compounds, or analogs. The magic aspect of silver halide photography is the amplification of the initial exposure which is obtained during development. Up to a million atoms of silver are obtained per incident photon. This amplification is possible only because silver metal is itself a catalyst for the devolopment of silver halides. This is a nearly unique aspect of silver redox chemistry.

The discussion above grossly oversimplifies the complexity of silver halide photographic chemistry. A more detailed discussion is beyond the scope of this review. The interested reader is referred to monographs on the topic [7]. More germane to the present review is the evolving picture of the electron transfer photochemistry which occurs during the spectral sensitization of silver halide materials.

Spectral sensitization was discovered in 1873 by Vogel [8]. It represents one of the most important discoveries enabling the development of modern photography. Addition of many organic dyes to silver halide emulsions resulted in extension of the photographic action to long wavelengths absorbed by the dye but not by the silver halide itself. It is of historical interest that the discovery of silver halide sensitization by dyes was nearly coincidental with the discovery by Becquerel of the sensitizatiion of the process of photosynthesis by chlorophyll [9].

Silver halide microcrystals are wide band gap semiconductors which exhibit weak photoconductivity. Early experiments demonstrated that dyes that sensitized silver halide photographic action also sensitized silver halide photoconductivity [6c]. Since the observation of photoconductivity necessitates the movement of free charge within the crystals, dye sensitization processes must inject charge into the silver halide lattice in some way. Initial theories of sensitization were based on the semiconductor view of silver halides, especially as espoused by Gurney and Mott [10]. Current ideas are based on thorough studies of the absorption spectroscopy and luminescence of silver halide emulsions and of adsorbed, sensitizing dyes, and the oxidation-reduction properties of the dyes at silver/silver halide electrodes [11].

Two mechanisms are possible for dye sensitization. In one, direct electron injection from the excited dye level into the conduction band of the silver halide occurs. An extensive series of experiments varying the relative positions of the dye HOMO and LUMO levels with respect to the silver halide valence and conduction band positions has established the validity of the direct electron injection model [11]. In this mechanism (Fig. 4), the dye molecular orbital levels (HOMO and

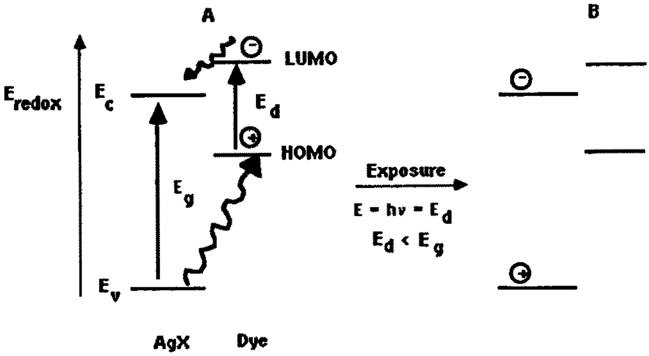


Fig. 4. Process of dye sensitization of AgX. *A* Light absorbed by dye and subsequent charge injection into AgX levels from dye levels; *B* final state has the same result configuration as if AgX was directly excited by light

LUMO) are positioned with respect to the silver halide valence and conduction band such that excitation of the dye, with light of energy too small to directly excite the semiconducting silver halide, provides an electron in the dye LUMO that is energetically above the conduction band of the silver halide. Injection of the electron into the semiconductor can occur only if the dye is surface adsorbed to the silver halide, and only if the dye is electronically coupled to the semiconductor. The latter is accomplished through the physics of Schottky-like barrier devices. Once the electron is injected into the silver halide, the hole remaining in the HOMO of the dye is quenched by removal of an electron from the (filled) valence level of the silver halide. The net result is indistinguishable from the result that would have been obtained by direct excitation of the silver halide with photons of greater energy. Obviously, the "extra" energy required to accomplish this sensitization with the low energy photon adsorbed by the dye arises from the redox energy stored during the excitation.

An alternate mechanism for spectral sensitization, not involving direct electron injection into the semiconductor, is energy transfer from the excited, adsorber dye to some unidentified acceptor state near the surface of the silver halide, followed by promotion of an electron into the conduction band. In an elegant series of

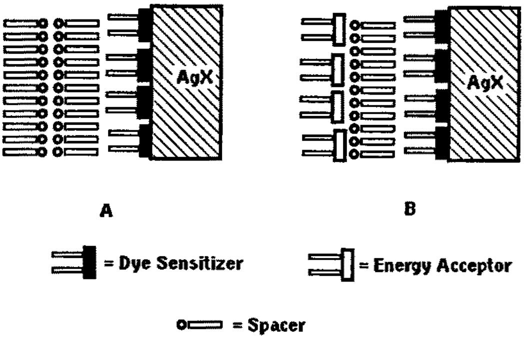


Fig. 5. Schematic diagram of dye sensitization of AgX as demonstrated by Kuhn and Möbius [12] using monlayer techniques

experiments using monolayer assembly techniques (Fig. 5) [12], it was shown that energy transfer was a feasible mechanism for sensitization for AgBr photographic activity [13]. When dye sensitizers were in direct contact with AgX (e.g., Fig. 5), efficient sensitization occurred, which is compatible with either electron injection or energy transfer. However, by the use of spacers between the dye and the AgX surface (not shown in Fig. 5), sensitization efficiency was lowered in a manner compatible with the energy transfer mechanism. When energy transfer acceptors are placed in the region of the dye sensitizer (Fig. 5), even direct contact sensitization could be quenched. Experiments with mixed monolayers containing electron traps in the region of the dye, in proximity to the dyed silver bromide surface, imply that electron injection is the preferred sensitization mechanism for the normal photographic situation, but that excitation transfer can compete under special circumstances.

4 Other Semiconductor-Based Systems

The principles of semiconductor photophysics used in silver halide imaging can be applied to other semiconductors. However, the photographic speed obtained with silver systems is usually lost, since it arises not from the act of creating the latent image, but during the development step in which external electrons are supplied to the system to reduce silver ions to silver metal. Nevertheless, several interesting systems have been reported.

Titanium dioxide and other transition metal oxides and sulfides, as well as various II–VI materials (CdS, ZnO, etc.) have been used in imaging in their capacity as wide band gap semiconductors. One of the most interesting of these systems is one described by the Itek Corporation (Lexington, Massachusetts, USA) in 1969 [14]. The outstanding feature of this system was its ability to provide a latent image, similar to silver halide, which could be amplified in a development process to produce a black and white image. This was, however, accomplished by using silver ions. The Itek "RS process" operated as illustrated in Scheme 1. Exposure of a film containing, e.g., TiO_2 to light below the band gap energy (E_g) produced electron/hole pairs [Eq. (1)] which remained viable for some time after

$$\text{Exposure} \qquad TiO_2 \rightarrow TiO_2^* \qquad \text{(latent image formation)} \tag{1}$$

$$\text{Decay} \qquad TiO_2^* \rightarrow TiO_2 \qquad \text{(e/h recombination)} \tag{2}$$

$$\text{Activation} \qquad TiO_2^* + Ag^+ \rightarrow TiO_2 \cdot Ag^+ \cdot Ag^0 \tag{3}$$

$$\text{Development} \qquad TiO_2 \cdot Ag^+ \cdot Ag^0 + \text{developer} \rightarrow TiO_2 \cdot Ag_n^0 \tag{4}$$

Scheme 1 [14]

the light was removed, but which decayed over time [Eq. (2)]. The exposed film was activated by dipping in a solution of silver ions, Ag^+[Eq. (3)], which caused deposition of small islands of silver metal onto the exposed microparticles of TiO_2. Subsequent development of the exposed grain occurred in a normal silver halide developer to form the final image, which consists of TiO_2 particles covered *in toto* by metallic silver [Eq. (4)].

The Itek process is based on the photophysical properties of n-type semiconductors such as TiO_2 which trap photoelectrons at their surface after light exposure. Photoholes are driven to the particle interior by the internal space charge field of the semiconductor. Addends to the solution which are capable, in a redox sense, of accepting the trapped electron can do so with several consequences. In the Itek process the surface adsorption of silver ions results in the plating of small islands of metal onto the surface. In other processes (*vide infra*), electron transfer to an added acceptor has other consequences. The Itek result predates application of this phenomenon to solar energy conversion using Pt deposition onto semiconductors to catalyze water splitting [15]. The photoreduction of silver ions by irradiation of ZnO suspensions was reported by Hada and coworkers [16].

An entirely different consequence of electron (or hole) transfer to addends is provided by semiconductor-sensitized decomposition of electron acceptors A-X (or electron donors, i.e., hole acceptors, D-Y) [17]. If organic molecules whose redox states (anion radical or cation radical) are unstable with respect to scission into a free radical and an ion [Eqs. (5, 6)] are adsorbed onto a wide band gap semiconductor such as TiO_2, etc., then back electron (hole) transfer can be inhibited, if the scission process is rapid.

$$\text{A-X} + e^- \rightarrow \text{A-X}^{-\cdot} \rightarrow \text{A}\cdot + \text{X}^- \tag{5}$$

$$\text{D-Y} - e^- \rightarrow \text{D-Y}^{+\cdot} \rightarrow \text{D}\cdot + \text{Y}^+ \tag{6}$$

This concept was used to initiate free radical vinyl polymerization in an imaging process to produce photoresists [17]. Electron acceptors were **p**-nitrobenzyl halides as well as other simple A-X systems whose anion radicals were short-lived and fragmented via reductive fragmentation as indicated in Eq. (5) [18]. Similarly, hole acceptors which undergo oxidative fragmentation [Eq. (6)] were employed, e.g., tertiary amines containing an *alpha* hydrogen atom. It was, in fact, found that the photopolymerization process, an extemely sensitive method of detecting the presence of free radicals, worked best if both the A-X and D-Y species were simultaneously present at the surface of the semiconductor. In this case (Fig. 6), photoelectrons and photoholes are both trapped, to form two free radicals, in a process which results in net radiationless decay of the semiconductor. The redox properties of the A-X and D-Y species used need to be matched with the conduction and valence level energetics of the semiconductor in order for polymerization to proceed [18].

Masuda [19] has used semiconductor-based electrodes in an imaging process. Photoelectrochemical oxidation of aromatics (aniline, phenol, etc.) at TiO_2 electrodes was found to change the hydrophilc/hydrophobic balance of the

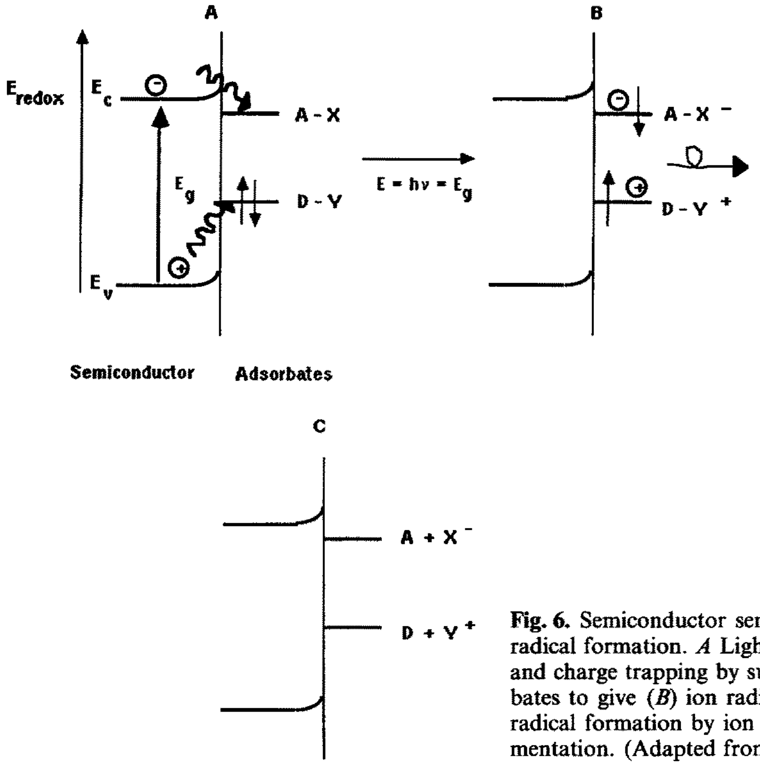


Fig. 6. Semiconductor sensitization of radical formation. *A* Light absorption and charge trapping by surface adsorbates to give (*B*) ion radicals. *C* Free radical formation by ion radical fragmentation. (Adapted from Ref. 17b)

electrode surface. This change in surface wettability by oily inks was used as the basis for a printing process. The photoelectrochemical process responsible for this surface modification was stated to be oxidative polymerization of the organic adsorbate on the TiO_2 surface, covering the exposed hydroxylic functionallity and rendering the exposed surface hydrophobic and ink-accepting.

An intriguing imaging system based on semiconductor photoredox was reported by Brinkman [20]. The imaging system involves a color change produced in sensitized PbO and other materials, but the process requires both thermal and photoactivation. PbO treated with triisopropanolamine is found to be insensitive to light at room temperature, but when irradiated at elevated temperatures (80–100 °C) the material turns dark, and the dark color remained when the sample was cooled. The image consists of fully reduced metallic lead.

A final imaging process which involves electron transfer in the family of semiconductor materials marries the concepts of dye sensitization of silver halides discussed earlier (Sect. 3) and the electron donor properties of n-type semiconductor particles presented immediately above. Levy [21] has found that intimate contact of semiconductor particles (PbO and related materials) with silver halide crystals can sensitize the photographic action of silver halides to wavelengths absorbed by the semiconductor. Using this method photographic systems of modest speed and remarkably low silver content can be produced. The principle is identical to dye sensitization in which electron injection into the silver halide conduction band occurs as the initial step leading to formation of the latent image, except here it is the semiconductor conduction band rather than the dye LUMO level which must be appropriately matched to the silver halide levels.

5 Electrophotographic Systems

Electrophotograhy, or xerography, was invented by Carlson in 1938, but the basic patent was not issued until 1942 [22]. Imaging using static electricity had been accomplished much earlier by Lichtenberg [23], but no practical image recording processes were feasible until Carlson's process was perfected in the 1950s. In its modern manifestation, xerography is practised in the following steps (Fig. 7). An electrically conducting substrate (S) is coated with a photoconductor layer (charge generation layer, CGL), which is usually overcoated with a dielectric layer containing a charge transport material (CTL). This three-layer structure is electrostatically insulating in the dark. Electrostatic charging is accomplished with a corana discharge apparatus (Step 1; in the figure, negative charging is shown for illustration). Exposure (Step 2), generates electron/hole pairs in the CGL which migrate in the applied electric field to the CGL/CTL interface and to ground (S) (Step 3a). The negative charge in the conductive substrate is removed to

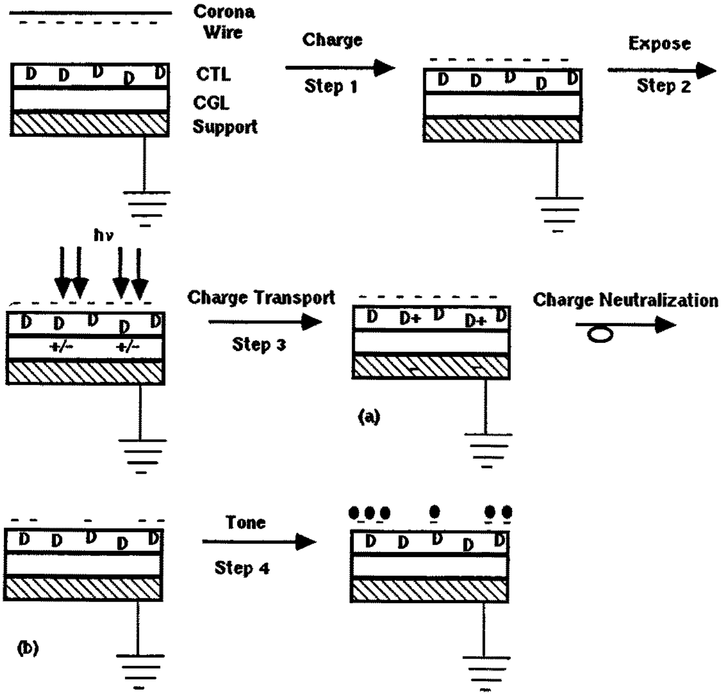


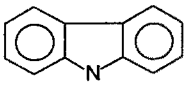
Fig. 7. Electrophotographic imaging process steps; see text for details

ground, and the positive charge at the CGL/CTL interface is injected across the interface into the CTL. The CTL consists of a glassy, polymeric phase doped with a hole donor (D, a reductant) in the case illustrated for negative corona charging. The hole donor acts as the charge-carrying species to transport charge to the originally charged surface (Step 3b) where it neutralizes the surface imagewise. The imaged surface is then toned (Step 4) with an electrostatic toner in pigmentary form. The final toned image is transferred to paper in conventional office copying [24]. Single layer compositions are also possible.

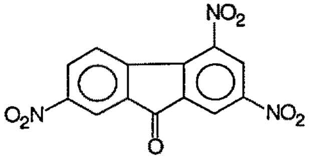
Several charge transfer processes operate in the xerographic process. As in the silver halide process (Sect. 3) and the imaging processes involving other semiconductor photoprocesses (Sect. 4), the primary photochemical event in xerography is formation of an electron/hole pair in the photoconductor. Many commercial xerographic copiers use amorphous selenium as the photoconductive material, but organic photoconductors have been used also. This review will be concerned only with the photophysics of the organic photoconductive materials that have been described in the literature.

The earliest all-organic photoconductive compositions consisted of polyvinyl(carbazole) (PVK, **1**) and 2,4,7-trinitrofluorenone (TNF, **2**) [25]. In spite of its historical importance, the PVK/TNF system is an unusual one, because it is one of the few photoconductors which acts simultaneously as a photogenerator of primary charges and the medium in which the charge transport is accomplished. It is much more usual to employ a separate charge generator and a distinct transport medium.

PVK itself is an inherent photoconductor under ultraviolet irradiation. The PVK/TNF pair constitutes a charge transfer complex, absorbing to the red of both components alone. Absorption of a visible photon in a thin layer of PVK doped with TNF generates a cation radical fragment in the PVK polymer chain, and an anion radical in the TNF fragment. The cation radical is mobile within the PVK chain. The TNF radical anion percolates through the glass by a self-exchange (hopping) mechanism. Thus the PVK/TNF system is bipolar, providing conduction of both electrons and holes (so that the surface could in principle be charged to be either positive or negative, and either sense of charging could be photodischarged). For PVK/TNF films (ca. 15 µm thick), absorption occurs in the bulk for visible irradiation. Charge carrier generation is limited by geminate recombination, and it has been found to be about 10% efficient at 550 nm when a 1 : 1 PVK : TNF composition is used [26]. One other charge transfer photoconductive composition has been reported. Goliber and Perlstein showed



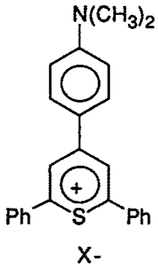
PVK, *1*



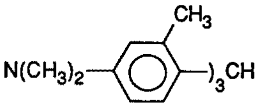
TNF, *2*

that the weak ground state CT complex between the donor triphenylamine and the acceptor, a borate inner salt, *B*, *B*-difluoroboron-1,3-diphenyl-1,3-propanedionate, can function as a viable photoconductor [27].

Only one other single-layer photoconductor compositon has proved practical. Kodak workers [28] have described compositions consisting of phase separated aggregates of a thiapyrillium dye (TPD, **3**) dispersed in a polycarbonate glass containing high levels (ca. 30–40% by weight) of triarylamine electron donors such as 4,4′-diethylamino-2,2′-dimethyltriphenyl-methane (LG-1,**4**).



TPD, *3*



LG-1, *4*

This photoconductive system is a remarkable composition. Phase separation of the microcrystalline TPD occurs apparently with inclusion into the polycarbonate crystalline regions. The crystalline photoconductor exhibits a strongly red-shifted and substantially sharpened absorption band compared to the TPD simply dissolved in the polycarbonate (Fig. 8). More interesting are the changes in photoconductivity of the aggregated vs the unaggregated compositons: the

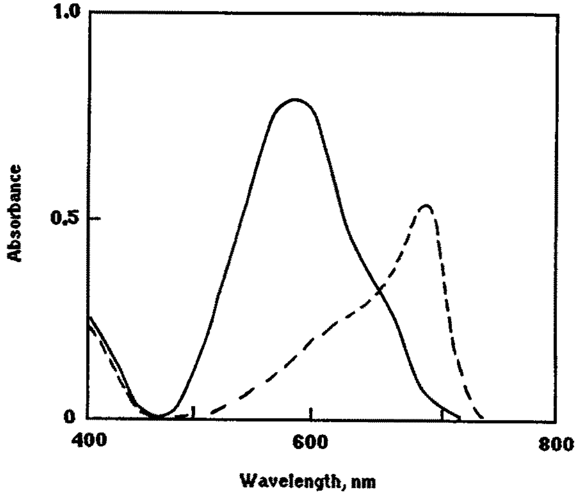


Fig. 8. Absorption of TPD (3) films in the homogeneous (———) and aggregated (– – – –) phase. (Adapted from Ref. 28a)

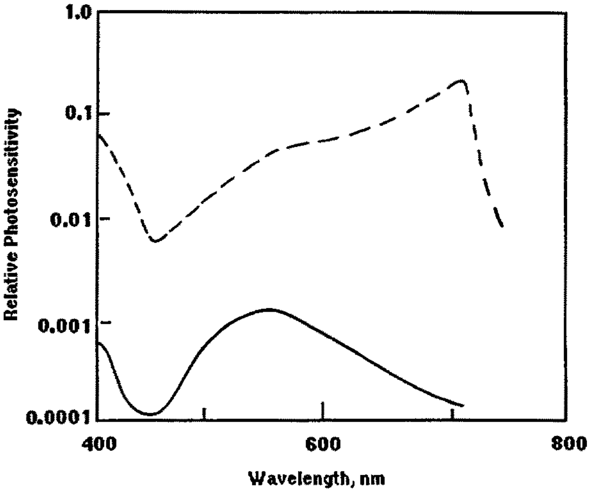
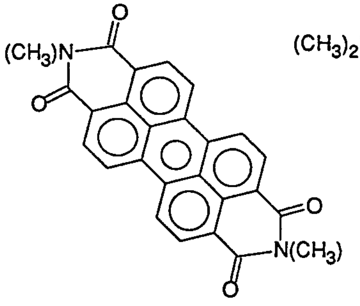


Fig. 9. Spectral response of photoconductivity of TPD (3) films in the homogeneous (———) and aggregated (– – – –) phase. (Adapted from Ref. 28a)

Kodak workers [28] reported a roughly 100-fold increase in the sensitivity of the compositions, at all wavelengths, on aggregation. Further, the aggregate was sensitive to red wavelengths unabsorbed by the unaggregated material. Figure 9 illustrates the data. The interpretation of the phenomenon is that the aggregated photoconductor behaves as a true semiconductor and is insulating in the dark, conductive in light. That is, true electronic conduction processes occur in the filamentary structure of the aggregated organic dye which are not possible in the glassy solutions, where only hopping transport mechanisms can be obtained.

In the Kodak system, which is substantially the composition used in the commercial Ektaprint® copiers, the arylamine (LG-1,4) acts as a source of holes, and is the hole transport medium. While the exact mechanism for carrier transport in this system is not known precisely, it is likely that electrons and holes are generated photochemically in the aggregate structure, separated spatially in the internal space-charge field of the film structure, and that holes are injected into the glassy phase of the composition by electron donation from LG-1 to the excited dye aggregate. Electron conduction occurs in the aggregate structure, and hole transport occurs normally by hopping in the LG-1 phase. Quantum yields of charge separation are as high as 0.6 in an electric field of 10^6 V/cm [28b].

Most organic photoconductors operate as two-layer systems in which the charge generation and charge transport functions occur in physically differentiable layers. The charge generation layer is normally a very thin (ca. 1 μm) pigment layer of high optical absorbance. Several organic photoconductors have been demonstrated to be effective [25]: phthalocyanines, both metal-free and metallated [29]; perylenes, such as *N,N'*-dimethylperylene-3,4,9,10-tetracarboxylic diimide (5) [30]; squarylium dyes, such as 2,4-bis(4'-dimethylamino-2'-hydroxyphenyl)cyclobutenediylium-1,3-dioate (6) [31]; and bis-azo pigments such as 3,3'-dichloro-4,4'-diphenylbis(1''-azo-2''-hydroxy-3''-naphthanilide) (7) [32, 39]. Each has properties suited for various applications, and each has been reported primarily in the patent literature. Detailed photophysical studies of the materials are generally lacking. Law has reported the emission properties of some squarylium dyes in solution and in the aggregate phase [33]. He has also reported interesting morphological effects of crystallite preparation on the photophysics and photoconductivity of these systems [34].



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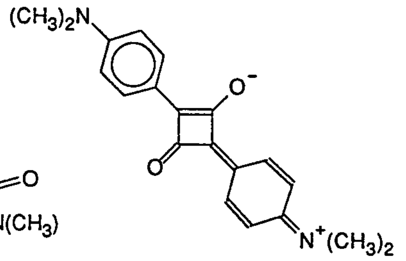

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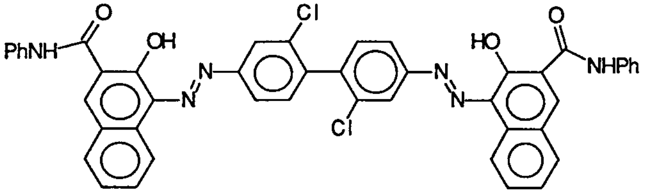

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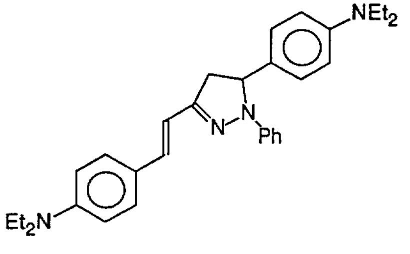
Molecules which function as charge transport materials, whether incorporated into single or double layer compositions, are chosen because of their redox properties. The electric field present during the xerographic imaging process drives the electron transport chain in the medium. Electron exchange occurs between charged molecules and their neutral parents, present in high concentration [35]. For compositions which are charged positively (that is, a positive corona charge is applied to the surface), negative ions must be transported to the surface. Radical anion species are normally supposed to be the carriers in such systems. TNF is one example [26]. Other nitroaromatics and malononitrile adducts of aromatic ketones like fluorenone constitute the bulk of other known electron transport materials [36]. For a series of cyanoaromatic electron transport materials the initial rate of photoinduced discharge of the compositions with PVK was shown to be well correlated with the reduction properties of the molecules in solution [37]. Traditionally, most electrostatic imaging systems are charged with a negative corona, so that the majority carrier for transport to the surface is a positive ion, usually a cation radical. Many more hole transporting materials are known than electron transporting ones. In addition to the amino-substituted triarylmethanes such as LG-1 described above for the use with TPD systems, other hole transport molecules include pyrazolines, e.g., 1-phenyl-3(4′-diethylaminostyryl)-5-(4″-diethylaminophenyl)pyrazoline [38] (**8**); hydrazones, such as *N*,*N*-diphenyl-4-dimethylaminobenzaldehyde hydrazone [39] (**9**); and heterocycles, especially oxadiazoles, e.g., 2,5-bis(4-*N*,*N*-diethylaminophenyl)-1,3,4-oxadiazole (**10**) [40]. For effective hole transport, low oxidation potential materials are desirable, but if the compound is too easily oxidized, trap centers can be introduced during corona charging steps.



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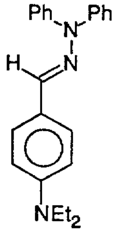

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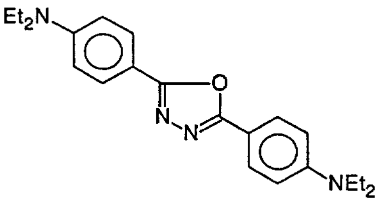


10

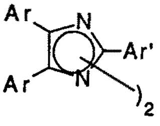
In all charge transport processes, several factors govern overall efficiency [25]. First, the generation of free carriers within the CGL is field dependent. Second, at the interface of the CGL and CTL, injection processes can be rate limiting. Finally, the mobility of the carriers in the CTL can be limiting. These factors are balanced delicately in functional electrophotographic systems to optimize performance-response characteristics. A full discussion is beyond the scope of the present chapter.

6 Color Formation Systems

It has long been a desire of photographic scientists to develop nonsilver systems capable of forming full color images rapidly and conveniently. A search for photochemical processes which result in the formation of colored products has been a mainstay of research to this end for many years. The goal has been elusive. To date, no simple organic photoprocess can compete effectively with the silver halide imaging process in photospeed (sensitivity). Several low amplification processes have been developed which are slower (less photosensitive) than the silver process, but they are in general not sensitive to visible light, but rather require ultraviolet sources. Dessauer and Looney have recently reviewed this area of image formation [41]. This section will emphasize such systems in which electron transfer processes play a role. Simple photochromic systems, unsensitized diazo systems, and others will not be considered.

Historically, the first color-forming reaction to be discovered which involves electron transfer is probably the photoinitiated reaction of diphenylamine with carbon tetrabromide, which forms blue colors [42]. In fact, the major path for color formation is due to radical reactions, initiated by photolysis of C – Br bonds to produce Br_3C and bromine atoms. An alternative mechanistic path, possible when the light is absorbed by the diphenylamine, would involve electron transfer. MacLachlan has shown that such processes do occur during photolysis of aminotriarylmethanes in the presence of electron acceptors such as CBr_4 and CCl_4 [43]. Other electron deficient species (quinones, nitroaromatics) were also demonstrated to be effective.

The oxidation of leuco triarylmethane dyes to their colored form is, of course, very old chemistry. Photoxidation has been used commercially in color-forming imaging systems such as the Photohorizon system (Horizons Chemicals) and Du Pont's Dylux®. These are complex systems which may not follow the paths outlined in simple model systems that have been studied and which are outlined below. However, they are significant commercial systems which deserve some separate comment. The Photohorizons systems produced color via photoxidation of amines initiated by polyhalogenated compounds generally. Dipnenylamine/CBr_4 is a prototype, but sensitizers such as tribromoacetophenone were also used. Various colors were produced by using appropriately substituted amines or aminotriarylmethanes. The photospeed of such systems were some 10^4 slower than silver halide photographic systems. In the Dylux® system, initiation of the color-forming process occurs after photolysis of a hexaarylbiimidazole (HABI, **11**) derivative. Electron transfer processes are unambiquous in this system, and will be discussed in some detail. Photospeeds are generally 10^6 slower than silver halide.



HABI, *11*

MacLachlan has examined the quenching of excited tris(4-diethylaminophenyl)methane (leuco crystal violet), **12**, by CCl_4 using both steady-state and transient techniques [43]. Both singlet and triplet quenching processes were observed. Diffusion-controlled electron transfer from excited leuco dye to CCl_4 was demonstrated to be initiation event. Quantum yields of color formation were measured and shown to be in the range 0.3–1.2 for $[CCl_4]$ from $0.005M$ to $0.1M$. Oxygen partially inhibited the photoxidation, an effect attributed to quenching of the triplet component of the reaction. The mechanism shown below in Scheme 2 [Eqs. (7–16); DH = leuco dye, **12**, D^+ = dye, **13**] accounts for MacLachlan's observations [43].

$$\mathrm{DH} + h\nu \rightarrow \mathrm{DH}^* \qquad (7)$$

$$\mathrm{DH}^* \rightarrow \mathrm{DH} + h\nu \qquad (8)$$

$$\mathrm{DH}^* \rightarrow \mathrm{DH}^*(\mathrm{T}) \qquad (9)$$

$$\mathrm{DH}^* \rightarrow \mathrm{DH} + \Delta \qquad (10)$$

$$\mathrm{DH}^* \text{ or } \mathrm{DH}^*(\mathrm{T}) + \mathrm{CCl_4} \rightarrow \mathrm{DH}^{+}\cdot + \mathrm{CCl_4^{-}}\cdot \qquad (11)$$

$$\mathrm{CCl_4^{-}}\cdot \rightarrow \mathrm{CCl_3}\cdot + \mathrm{Cl^-} \qquad (12)$$

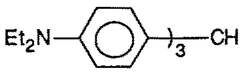
$$\mathrm{DH} + \mathrm{CCl_3}\cdot \rightarrow \mathrm{DH}^{+}\cdot + \mathrm{CCl_3^-} \qquad (13)$$

$$\mathrm{DH}^{+}\cdot + \mathrm{CCl_4^{-}}\cdot \rightarrow \mathrm{D^+} + \mathrm{HCl} + :\mathrm{CCl_2} + \mathrm{Cl^-} \qquad (14)$$

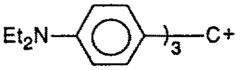
$$\mathrm{DH}^{+}\cdot \rightleftharpoons \mathrm{D}\cdot + \mathrm{H^+} \qquad (15)$$

$$\mathrm{DH}^{+}\cdot + \mathrm{D}\cdot \rightarrow \mathrm{D^+} + \mathrm{DH} \qquad (16)$$

Scheme 2



12 (DH)



13 (D+)

Key steps of the mechanism are electron transfer quenching of Eq. (11), which can occur in either the singlet or triplet state, fragmentation of the anion radical as in Eq. (12), and various steps which lead to dye, especially the disproportionation step of Eq. (16), which is facilitated by the stability of triarylmethane radicals. The reaction steps of Eqs. (15, 16) represent the process thought to contribute most of the observed product. The cation radical $DH^{+}\cdot$ was observed experimentally by low-temperature ESR as well as by flash photolysis. The product D^+ (**13**) is blue and absorbs at 590 nm.

The Dylux® system operates somewhat like the above photoxidation of leuco crystal violet, but the initiation step is different. Triarylimidazolyl radicals are generated by ultraviolet (365 nm) irradiation of their stable dimers (HABI's: hexaarylbiimidazoles, **11**) [44]. The persistent free radicals (called lophyl radicals because they were historically derived from the parent *lophine*, triphenylimidazolyl dimer) produced are capable of oxidizing leuco dyes such as leuco crystal violet, among other low-ionization potential species [45]. Equations (17, 18) [46] delineate the mechanism for redox reactions schematically, illustrated for a generic triarylimidazolyl dimer (L_2, L = lophyl) and oxidation of a leuco dye, DH. Color formation occurs analogously to Eqs. (15, 16) above. Substrates demonstrated to be subject to single

$$L_2 + h\nu \rightarrow 2L\cdot \tag{17}$$

$$L\cdot + DH \rightarrow L^- + DH^{+\cdot} \tag{18}$$

electron transfer to lophyl radicals (L·) include dialkylanilines (diethylaniline, $k_{ET} = 4 \times 10^4\ M^{-1}\ sec^{-1}$; *N,N*-dimethyl-*p*-toluidine, 2×10^6; *p*-cyano-*N,N*-dimethylaniline, 3×10^2), leuco dyes of the triarylmethane class (tris-(*p*-diethylaminophenyl)methane, $k_{ET} = 4 \times 10^6\ M^{-1}\ sec^{-1}$), and aromatic diamines (*N, N, N′, N′*-tetramethyl-*p*-phenylenediamine, $k_{ET} = 4 \times 10^7\ M^{-1}\ sec^{-1}$). Here, rate constants for electron transfer were determined by flash photolysis and are stated on the basis of a rate "per-amino" function present in the molecules described [44]. In further support of electron transfer pathways for the oxidation of amines by lophyl radicals, Cohen [47] observed by flash photolysis that the rate was accelerated by the presence of electron-withdrawing substituents in the aryl rings of the 4- and 5-aryl substituents, and slowed by electron-releasing substituents. Cohen also observed an interesting steric acceleration to electron transfer in 2-(*ortho*)-substitued aryl groups in the L· series containing *ortho* halogens (H vs F, Cl, and Br) [47]. It was noted that the rates of oxidation of leuco green 1 (LG-1; tris-(2-methyl-4-*N,N*-diethylaminophenyl)methane, 4) increased linearly with the van der Waals radius of the 2-(*ortho*)-substituent. Apparently, twisting the 2-aryl ring out of plane to the imidazolyl ring increases the electron-accepting ability of the radical, since strong polar effects would not be anticipated in the series F, Cl, Br.

In the Dylux® process, the oxidized leuco dye is the source of color in the final product. Because the color is formed in a molecular process, the optical density of dye produced is directly proportional to the light dose absorbed. That is, the imaging system operates in a continuous tone manner, and faithfully reproduces light variations incident upon it. Since the light-sensitive materials (HABI dimer and leuco dye) are still present in the unimaged areas (or underexposed areas) of the film (or impregnated paper), second images may be added, to update the information added initially. On the other hand, this means that an exposed film is not "fixed" toward unwanted light exposure. Dessauer has devised elaborate secondary exposure techniques to produce redox inhibitors to prevent such post-exposure fogging of Dylux® papers (see Ref. [40] for a full discussion of this chemistry). Imaging papers such as Dylux® are used industrially as blue-print equivalents and as "proofing" papers in the graphic arts industry to preview the quality of photographic intermediates in the printing process.

A final electron transfer-based color formation system is an inorgaic one. In a series of patent publications, DoMinh of Eastman Kodak describes a high amplification system for color formation based on the photoredox reactions of Co(III) amine complexes [48]. Color formation is provided by the classic reaction of an aromatic dialdehyde with an amine [49]. The amines are produced by reduction of aminocobalt (III) complexes to the cobaltous state in aqueous media in which aquated cobalt (II) is thermodynamically favored. Thus, the amine ligands are efficiently and irreversibly lost on photoredox. Since up to six amino ligands can be released per photon, and since the reactions to form dyes have the added advantage of producing highly colored species, high gain systems are possible. Photospeeds approaching those of silver halide systems were reported [48]. Direct photoredox of the cobalt complex in the presence of weak reducing agents (or reducing counterions) can be effected, or quinones can be used as mediators, during which photoreduction of the quinone by normal hydrogen abstraction chemistry provides hydroquinones capable of reducing the inorganic species in thermal processes.

7 Photopolymerization Systems

Photopolymerization is traditionally initiated by direct photolysis of a precursor to provide free radicals via bond homolysis. Examples of such initiators include benzoin, and benzoin ethers, disulfides, and azoalkanes or dialkylperoxides. Hydrogen abstraction chemistry, typified by benzophenone photochemistry, is also recognized as extremely useful. However, a number of viable commercial photopolymer imaging systems are based upon ionic (especially cationic) polymerization. These systems will be discussed next.

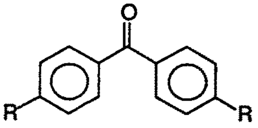
Among the most ubiquitous photoredox free-radical initiators, and the one of most familiarity to organic photochemists, are those based on quenching of ketone triplet states by amines containing *alpha*-hydrogens [3, 50]. Aryl ketones, exemplified by benzophenone (BP, **14**), are quenched by secondary or tertiary amines containing at least one hydrogen atom *alpha* to the amino nitrogen by the mechanism outlined in Eqs. (19, 20). A charge transfer exciplex is

$$\mathrm{BP^*(T)} + \mathrm{R_2N(CH_2R')} \rightarrow \mathrm{BP^{-}\cdot} + \mathrm{R_2N^{+}\cdot(CH_2R')} \qquad (19)$$

$$\mathrm{BP^{-}\cdot} + \mathrm{R_2N^{+}\cdot(CH_2R')} \rightarrow \mathrm{BPH\cdot} + \mathrm{R_2N(CHR')} \qquad (20)$$

implicated. Electron transfer to the excited triplet, according to Eq. (19), produces a radical ion pair. Proton transfer, from the carbon *alpha* to nitrogen, to the ketyl anion radical oxygen atom, gives a pair of radicals [the BP ketyl radical and the α-amino radical, Eq. (20)]. The ketyl radical is not sufficiently reactive to initiate polymerization, but the α-amino is a potent initiator.

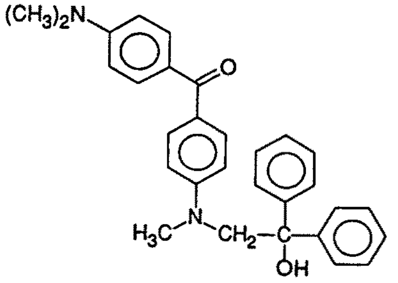
The efficacy of various amines in this electron-transfer-initiated process is governed by several factors [51]. While the ionization potential of the amine is obviously important, substituents present on the carbons *beta* to the nascent radical center also play a role. Thus, it has been shown that dimethylaniline is less effective than is triethylamine, and that triethanolamine is among the most effective coinitiators [50].



R = H, *14*, BP
R = N(Me)2, *15*, MK

Other aryl ketones function similarly with amines to produce coinitiating pairs of materials which together function via electron transfer. One would not anticipate, however, that Michler's ketone (bis-4,4'-dimethylaminobenzophenone, MK, **15**) would act in any special manner as an electron acceptor partner in this sense, and such is the case. However, it was found serendipitously [52] that the *combination* of MK and BP together was an especially (in fact synergistically) effective combination, and that no added amines were required. Photospeed enhancements observed in some photopolymer compositions were impressive: with BP alone, photospeeds were enhanced 3-fold by addition of triethanolamine; with MK alone, photospeed was lower that with BP alone (0.3 ×), and addition of triethanolamine did not enhance the photospeed greatly (0.5 × BP), but the combination of MK and BP (no amine) had photospeed 14 × BP alone [53]. The α-amino radical derived from MK by electron transfer followed by proton loss is implicated from end-group analysis experiments. The MK/BP pair remains among the best photoinitiators of radical processes known to date.

Hammond, Wamser, Chang, and Baylor [54] studied the photochemistry of the BP/MK pair formally using flash photolysis techniques and showed that electron transfer occurs via triplet exciplexes that can be formed by excitation of either partner, though under normal circumstances MK absorbs the vast majority of the light. Benzophenone ketyl radical was observed as a transient, and a second species present was identified as either the cation radical of MK or its corresponding deprotonated radical. The coupling product of the latter two radicals (**16**) was observed as a product of steady-state irradiation, and it was formed with a quantum



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yield of 0.079, even in *iso*-propanol as solvent. The observed quenching of excited triplet MK by BP occurred with a bimolecular rate constant of 8×10^6 M^{-1} sec^{-1}. The triplet energy of BP is above that of MK by some 7–8 cal/mol, so that only electron transfer processes are energetically feasible.

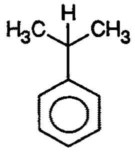
The lessons learned from the photophysical study of the BP/MK system influence methods to optimize photopolymer imaging systems. Since MK absorbs most of the light in this system, one wishes to optimize the amount of MK used for the thickness of the photoimaging composition, but the self-quenching of MK should also be minimized. Since the BP functions basically as a quencher, its concentration should be as high as is practicable [51].

Another initiator system that can operate using electron transfer pathways involvers the HABI's discussed above in connection with color formation systems (see Sect. 6). Lophyl radicals were shown to be able to oxidize various leuco dye species to their colored forms. Similarly, such radicals can extract an electron from an arylamine containing hydrogens on a carbon *alpha* to *N* to form α-amino radicals capable of initiation [Eqs. (21, 22)] of

$$L\cdot + R_2N(CH_2R') \rightarrow L^- + R_2N^{+}\cdot(CH_2R') \qquad (21)$$

$$L^- + R_2N^{+}\cdot(CH_2R') \rightarrow LH + R_2N(CHR) \qquad (22)$$

vinyl polymerization [44, 55]. The lophyl radical is also capable of direct hydrogen atom abstraction from coinitiators such as thiols to form initiating radicals. Rates of hydrogen atom abstraction are limited to *circa* 10^4–10^7 M^{-1} sec^{-1} since abstraction is inherently an activated process. Electron transfer processes can in principle occur at diffusion encounter limited rates, near 10^9–10^{10} M^{-1} sec^{-1}. During the 1970s, we [56] undertook a model study to determine if interactions of lophyl radicals with coinitiators commonly thought to proceed *via* H-abstraction could in fact occur *via* electron tranfer pathways. Absolute rates of methyl methacylate polymerization initiated by bis(2-*o*-chlorophenyl-4,5-diphenylimidazolyl) (*o*-CL-HABI, **11**, Ar = Ph, Ar′ = *o*-ClC_6H_5) in combination with various coinitiators were measured and compared to rates of systems whose mechanism of intiation could be certainly known. Compounds chosen which would operate purely *via* H-abstraction were cumene (**17**) and the ethylene ketal of benzaldehyde (**18**). Models for pure electron transfer were dimethylaniline and the potassium salt of *p*-toluenesulfinic acid (**19**) (studied as its complex with the polyether 18-crown-6 for solubility purposes). These results were compared to those for coinitiators of "ambiguous" mechanism: triethylamine, the heterocyclic mercaptans 2-mercaptobenzoxazole, (2-MBO, **20**), 2-mercaptobenzimidazole (2-MBT, **21**), and 2-mercaptobenzthiazole (2-MBT, **22**), and the disulfide of 2-mercaptobenzthiazole (2-MBT dimer, **23**). In this way, 2-MBT was judged to initiate predominantly *via* electron transfer pathways, with a rate of electron transfer between the *o*-Cl-HABI derived lophyl radical and 2-MBT approaching 2×10^9 M^{-1} sec^{-1} in benzene solvent ($K_{dif} = 10^{10}$ M^{-1} sec^{-1}). Initiation rates by the other heterocyclic thiols were 60–70% that of 2-MBT. Competition between H-atom abstraction and electron transfer can occur in these systems. These studies demonstrate that coinitiation systems can be exceedingly complex, and that multiple mechanisms may arise.



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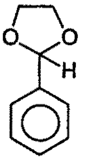

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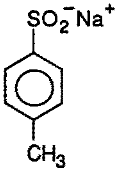

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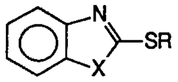

20, R = H, X = O, 2-MBO
21, R = H, X = N, 2-MBI
22, R = H, X = S, 2-MBT
23, R = *22*, (where R is absent), X = S, (2-MBT Dimer)

Onium salts such as triarylsulfonium and diaryliodonium can initiate both free radical and cationic photopolymerization [57]. Direct photolysis, effective only for wavelengths below about 260 nm, produces phenyl radicals and cation radicals as illustrated in Eqs. (23, 24). Because these systems absorb

$$Ph_2I^+ + h\nu \rightarrow PhI^{+\cdot} + Ph\cdot \qquad (23)$$

$$Ph_3S^+ + h\nu \rightarrow Ph_2S^{+\cdot} + Ph\cdot \qquad (24)$$

only in the deep UV, it has been necessary to devise sensitization methods to enable use of longer wavelength light sources. Electron transfer pathways are normally indicated for these processes, since most visible sensitizers are incapable of exothermic energy transfer to either onium substrate. For example, singlet anthracene has been shown to initiate electron transfer sensitization with the onium salts [56c]. The onium salt functions as an electron acceptor [Eqs. (25, 26)]. Back electron transfer within the geminate [Eq. (27)] competes with effective sensitization of radical formation. Dyes such as bis-(*p*-*N*,*N*-dimethylaminobenzylidene acetone) are also effective sensitizers in the visible

$$Ph_2I^+ + Anth^* \rightarrow Ph_2I\cdot + Anth^{+\cdot} \qquad (25)$$

$$Ph_2I\cdot \rightarrow PhI + Ph\cdot \qquad (26)$$

$$Ph_2I\cdot + Anth^{+\cdot} \rightarrow Ph_2I^+ + Anth \qquad (27)$$

region (though in this case, triplet dye acts is the active sensitizing species) [56c].

For nearly all photopolymerizations initiated by absorption of light in the visible region, electron transfer is the only viable mechanism. A family of visible dye sensitizers has been examined over 30 years and shown to be ubiquitous as acceptors of electrons from a variety of electron donors. The area has been recently reviewed [58], and will not be discussed comprehensively here.

The family of photoreducible dyes (*e.g*, acridinium, xanthene, thiazinium among other classes of dyes) produce excited states of essentially quinoidal structures which can act as efficient acceptors of electrons. Amines [59], sulfur compounds, especially sulfinate salts [60], heterocycles of low ionization potential [61], alkylcarboxylates and stable enolate anions [62], and several classes of organometallic compounds, notably allylic and benzylic organostannanes [63], represent classes of compounds which have proved efficacious as coinitiators in electron transfer sensitization with these dyes. Electron transfer with the organometallics was unambiguously established in a series of model studies involving electron acceptors of the anthracene class [64].

The dye-sensitized systems suffer one drawback which has prevented their use: ground-state charge transfer complexation between dye and the reductant can result in slow dark reactions which deplete the dye and/or the reductant. A method to avoid this problem was devised by workers at Mead Imaging [65]. In the Mead system, used to produce color images using visible sensitizers to both initiate photopolymerization and photooxidize a leuco dye inside tiny polymeric microcapsules [66], the dye sensitizer and coinitiating reducing agent are contained together in a salt, D^+X^-, in which D^+ is a cationic photoreducible dye and the counterion X^- has an ionization potential such that redox occurs only on photoexcitation. The counterion X^- is chosen such that the oxidized form ($X\cdot$) is unstable with respect to fragmentation. The basic photochemistry of the D^+X^- pair has been investigated by Schuster, who reported direct transient spectroscopic measurements of the electron transfer reactions of the borate salts of cyanine dyes [67], and who also studied the redox photochemistry of an intermolecular model system (quenching of 1,4-dicyanonaphthalene by alkyltriphenylborate salts) [68]. Direct evidence for oxidative fragmentation of the borate anion was found. Analogies exist between the photooxidation of the borate salts and other irreversible redox couples such as the organostannanes [18b, 62, 63]. For the alkyltriphenylborates, removal of an electron produces an unstable radical, which fragments to give stable triphenylborane and an alkyl radical [Eq. (28)]:

$$RBPh_3^- + [Ox] \rightarrow RBPh_3\cdot \rightarrow R\cdot + Ph_3B \qquad (28)$$

In the case of photoinitiation of radical formation the generic oxidant, [Ox], is the excited state of the dye D^+, which is reduced during the process to the relatively stable radical for $D\cdot$ which is not an initiator, but which probably disproportionates in a bimolecular process.

8 Conclusions

Electron transfer pathways can play a vital role in photoinitiated pathways that lead to radicals or ions capable of initiating addition polymerization processes or which are important intermediates in other imaging processes. As the world in which we live and work moves rapidly toward an information-based society, dissemination of images from computer data bases, output from sophisticated laser-driven image writers, will become more pervasive. The need for new image formation processes which can respond to laser sources in the visible and infrared regions of the spectrum will become more acute. Electron transfer based imaging systems represent one response to this growing need.

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