



Figure 8. Consumption of industrial explosives in the U.S. from 1920 to 1980.

dustry Surveys, 1961-1981). Figure 8 shows this large increase in comparison with the previous 40 years. The recent economic conditions have hit the mining and construction industries very hard, resulting in a leveling off, or even a slight decrease, in explosives consumption the last few years. However, continued growth is expected to resume as the economy picks up. Since coal mines consume the majority (58%) of all explosives in the United

States and are the largest (33%) single market for slurries, a stable production volume base seems assured given the country's insatiable appetite for energy.

The improvements in slurry formulations and the development of emulsion explosives have made these products safer, easier, and cheaper to manufacture.

Recent developments have broadened the range of application of these products and improved their end-use characteristics so they are now being considered for a number of military applications as well as the more traditional civilian work. Successful use has already been demonstrated in certain bomb and missile fills, tank traps and trenching devices, and nuclear simulation charges. New and varied applications in government areas besides military, such as space and forest service, can also be expected under the influence of economic and technical competition.

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Chemistry of (5-Cyanotetrazolato- N^2)pentaamminecobalt(III) Perchlorate and Similar Explosive Coordination Compounds

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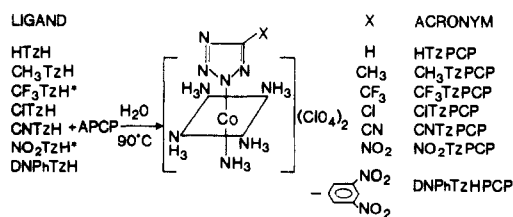
The coordination compound (5-cyanotetrazolato- N^2)pentaamminecobalt(III) perchlorate has been developed for explosive applications. Chemical studies applying to this development are reviewed. These include establishment of a commercial synthetic procedure, determination of structure, characterization of impurities, and development of analytical techniques for chemical analysis. Chemical reaction paths leading to impurity formation and associated with thermal decomposition are examined. The status of an ongoing effort to define relationships between chemical structure and explosive properties is presented.

Introduction

An extensive research and development program was undertaken to develop a safe explosive material that could be initiated by a thermal source and would exhibit rapid deflagration-to-detonation transition (DDT). The result was the synthesis and characterization of the high-energy coordination compound (5-cyanotetrazolato- N^2)pentaamminecobalt(III) perchlorate (CP). This paper reviews a variety of chemical studies that have been part of the program. While the emphasis is on CP, studies that have involved related compounds are included.

The application of interest was low-voltage detonators that can be thermally initiated by an electrical current passed through a resistive bridgewire. A generalized CP detonator is shown schematically in Figure 1. The igniter charge is initiated by the hot bridgewire, and growth to detonation occurs in the transfer column. The explosive charge is loaded in a series of increments under different conditions in order to maximize the desired functional characteristics in each of the column regions (Lieberman

Scheme I^a



^a Tz, tetrazolato; DNPh, 3,5-dinitrophenyl. * Generated in situ from sodium salts and HClO₄.

et al., 1981). The development of CP for this application represents a safety improvement over the prior use of primary explosives, such as lead azide. As shown in the generalized Table I (Lieberman and Fronabarger, 1979), CP has sensitivity characteristics that are different from those of common primary and secondary explosives. Clearly, a material that uniquely fulfills the requirements

Table I. Qualitative Comparison of CP with the Primary and Secondary Classes of Explosives

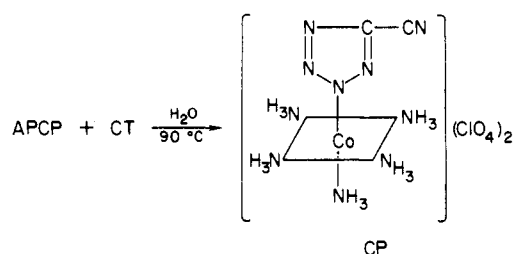
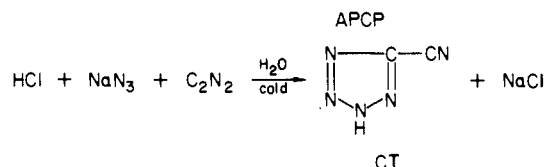
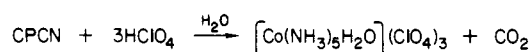
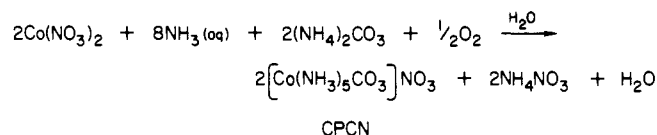
explosive type	sensitivity of unconfined materials to various stimuli			examples
	shock	electrostatic discharge	hot wire	
primary	sensitive	sensitive	sustains rapid reaction, often proceeds to detonation	lead azide
secondary	insensitive	insensitive	does not sustain reaction or burns in a slow manner	TNT ^a RDX ^a PETN ^a
CP	insensitive in bulk form, sensitive in unconfined pressed state	insensitive in bulk form, sensitive in confined pressed state	does not sustain in bulk form, sustains detonation in confined pressed state	

^aIncreasing sensitivity in the order TNT < RDX < PETN.

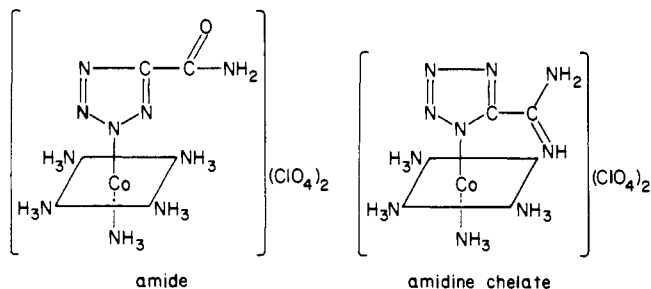
of specific explosive applications has resulted from coordination chemistry.

Synthesis and Characterization of CP

The synthesis of CP is performed via a batch process described by Fleming et al. (1979). The four steps are summarized below:



The bonding position of the tetrazole ring to the cobalt atom was determined by NMR analysis of labeled compounds (Balahura et al., 1983). A single-crystal structure determination by Graeber and Morosin (1983) also verified that the compound was N-2 bonded and established bond lengths. Analytical studies indicated that two other coordination compounds were present in the product as contaminants. They were subsequently identified as an amide and an amidine chelate of CP, as shown. The



former was identified by infrared spectroscopy and the latter by a single-crystal structure determination (Graeber and Morosin, 1983). Because the amide is highly insoluble, it was not possible to grow a crystal suitable for a single-crystal structure determination. For that reason the identification of the N-2 bonding position is assumed,

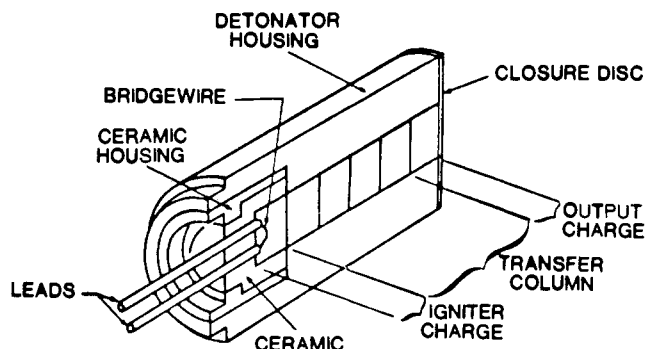


Figure 1. Generalized CP detonator design.

Table II. Analytical Results

parameter	typical values (theor)	analytical method
ClO_4^-	45.3–45.6% (45.5%)	gravimetric as tetrapentylammonium perchlorate
Co	13.6–13.7% (13.5%)	gravimetric as electrolytic metal
amide complex	1.5–3.5%	IR of carbonyl in deuterated amide complex
pH	5.6	glass electrode
Cl^-	<30 ppm	specific ion electrode
NH_4^+	<30 ppm	specific ion electrode
NO_3^-	100–250 ppm	spectrophotometric as diphenylbenzidine
CN^-	n.d.	starch/iodine titration
trace metals	≤0.02%	spectrographic on sulfated sample
moisture content	0.05%	mass loss at 100 °C
moisture uptake	0.15%	mass gain at 98% RH
surface area	0.42–0.51 m ² /g	BET with krypton

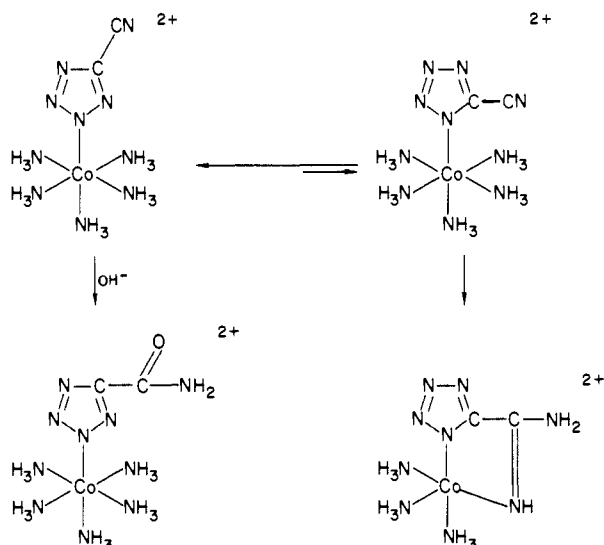
rather than proven, for this compound.

Typical analytical results are given in Table II. The major impurity in CP is the amide. While analysis of the amidine chelate is not routinely performed, its concentration is nominally an order of magnitude lower than that of the amide. Concentrations of common ionic impurities are low, typically below several hundred parts per million for those in greatest abundance. Techniques for the analysis of chloride, ammonium, and cyanide ions have been established by Merrill (1978). Several different techniques for the determination of amide content have been developed. Initially, thin-layer chromatography was used to provide semiquantitative data. Jungst and Peterson (1978) developed an analysis procedure based on the infrared spectrum of the deuterated material. Loyola and Womelsduff (1981) established a quantitative method based on the high-pressure liquid chromatographic analysis of the free ligands obtained as reaction products of the material with zinc amalgam. Schumacher and Bullock (1983) developed an alternative HPLC procedure that analyzed the complexes directly on a polyamide column.

Another species of concern is the Co^{2+} ion. Thermal decomposition studies by Searcy and Shanahan (1978) have shown that this ion forms early in the decomposition process. As a result, it is a sensitive measure of the stability or compatibility of CP in various environments. Merrill (1980) developed a spectrophotometric procedure for Co^{2+} based on the analysis of the CoCl_4^{2-} ion. Schumacher et al. (1985) developed a more sensitive spectrophotometric technique based on Co^{2+} complex formation with 2,2'-dipyridyl-2'-pyridylhydrazine.

Chemical Reactions

Mechanisms associated with the formation of impurities of CP have been of interest. The formation of the amide is assumed to be a simple hydrolysis reaction. For that reason it is believed that the ligand remains bonded in the N-2 position. The amidine chelate, however, has been shown to be N-1 bonded, which implies that the cyanotetrazole ligand may be at least partially N-1 bonded in solution. This has led to the following proposed sequence of reactions to account for the observed products:



The formation of the amidine chelate through this reaction sequence implies the existence of an N-1 bonded isomer of CP. None has been isolated or observed. Ellis and Purcell (1982), however, have shown that azide attack of [(substituted-nitrile)pentaamminecobalt(III)] complexes yield N-1 bonded [(substituted-tetrazolato)pentaamminecobalt(III)] complexes that are thermodynamically less stable than their N-2 bonded isomers. They have shown that increasing temperature and acidity accelerates the conversion of the N-1 to the N-2 form in solution. Since the process for the synthesis of CP involves both elevated temperature and acidic conditions, the formation of the N-2 isomer is consistent with the findings of Ellis and Purcell (1982). Most importantly, their work provides a basis for assuming that an N-1 isomer of CP can exist, which is the cornerstone of the reaction sequence leading to the formation of the amidine chelate.

Using the analytical techniques developed for the analysis of impurities in CP and mass spectrometry, Searcy and Shanahan (1978) characterized the thermal decomposition process as consisting of three general stages. The first stage is endothermic and involves the dissociation of ammonia. It appears to include the reduction of Co(III) by ammonia to yield Co(II) and gaseous nitrogen. Cleavage of the tetrazole ring occurs with the evolution of nitrogen. The second stage is exothermic and involves reaction of the perchlorate anion with ammonia and partial oxidation of cyanotetrazole. It occurs in parallel with the first stage.

The final stage includes additional consecutive redox reactions and occurs in parallel with the prior stages. The overall reaction sequence is very complex and includes many individual reactions occurring both in series and in parallel. Yelton et al. (1984) utilized a variety of mass spectrometric and ancillary techniques to more closely examine the early-stage thermal decomposition processes. They showed that ammonia is definitely the first gaseous product evolved. The identification of cyanogen and nitrogen indicated that ring opening was occurring. On the basis of bond lengths determined by Graeber and Morosin (1983), it was proposed that the ring bonds between N-1 and N-2, and N-3, and N-4 and C-5 were cleaved to yield the observed gases. Attempts to identify the parent molecule by mass spectrometry were unsuccessful.

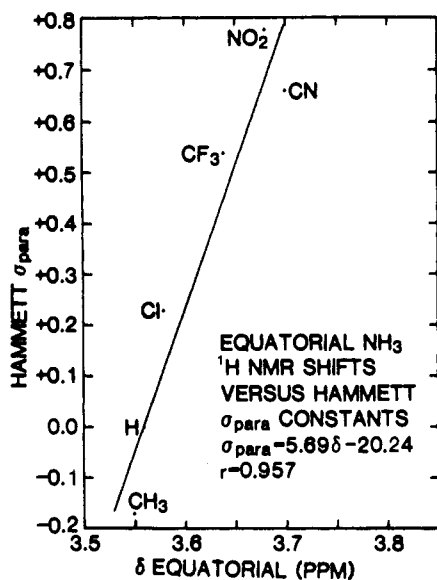
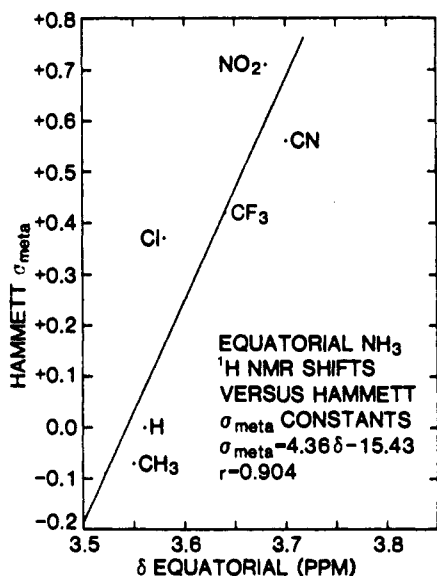
The identification of ammonia as the initial gaseous product of thermal decomposition raises the question as to whether evolution occurs preferentially from the equatorial or axial ammines. One approach to answering this question is via mass spectrometry of isotopically labeled compounds. The axial ammine could be distinguished from those in the equatorial positions by having the former either fully deuterated or ^{15}N labeled. This approach is under current investigation. In a related study Lieberman et al. (1984) showed by proton and deuterium NMR spectroscopy of partially deuterated CP samples that deuteration occurs preferentially in the axial position, but deuteration of equatorial ammines precedes complete deuteration of the axial ammine. As a result, complete deuteration of the axial ammine without deuteration of equatorial ammines requires an alternative synthetic route rather than controlled partial deuteration of CP.

Chemical Tailoring

Lieberman and Fronabarger (1980) reviewed the status of the development of CP in 1980. Whereas as a loose powder CP is insensitive to a human-body-equivalent electrostatic discharge, it is not insensitive to such a stimulus when loaded and pressed in detonator hardware. Therefore, the safety improvement that exists with regard to the handling of loose powders does not exist with regard to the handling of detonators; i.e., a spark can ignite the compressed powder and yield a detonation. As a result, spark protection devices are incorporated in such detonators. The ultimate goal is to develop a material that provides electrostatic safety whether as a loose powder or as a compressed material in a detonator. This has led to ongoing studies that attempt to determine the factors that affect spark sensitivity. Clearly, this parameter is affected by both chemical and physical variables. One approach that has been taken is based on chemical "tailoring" of CP. It involves selectively replacing chemical moieties of the molecule and evaluating the resultant electrostatic and detonator properties.

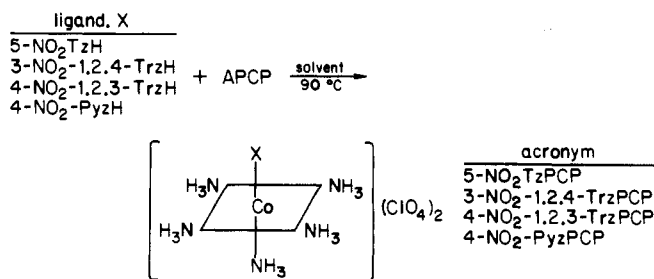
In one study Fleming et al. (1980) synthesized and characterized a series of CP analogues in which the cyano group was replaced by groups of various physical sizes and electron-withdrawing character. The syntheses are summarized in Scheme I.

In unpublished work Morosin has established that the compounds with the methyltetrazole and (dinitrophenyl)tetrazole moieties have N-2 bonding of their tetrazole rings to the cobalt atom. Since CP is also bonded in this position and these three compounds cover the range of size and electron-withdrawing character of the moieties considered, it is reasonable to infer that all of the compounds listed above are N-2 bonded. As part of the characterization of these compounds, Fleming et al. (1980) attempted to correlate proton NMR shifts with Hammett

Figure 2. Hammett σ_{para} values.Figure 3. Hammett σ_{meta} values.

σ constants, as shown in Figures 2 and 3. Subsequent performance testing by Fronabarger et al. (1981) indicated that increasing electrostatic sensitivity and increasing ease of growth to detonation correlated with increasing electron-withdrawing ability of the moiety.

In another study Fleming et al. (1982) synthesized and characterized nitroheterocyclic pentaamminecobalt(III) perchlorates. The heterocyclic groups were the tetrazolato (Tz), both triazolato (Trz), and the pyrazolato (Pyz) moieties. The purpose of this investigation was to obtain materials with which to evaluate the effect of ring composition on resultant performance properties. The syntheses are summarized below.



For 3-NO₂-1,2,4-TrzH, the solvent used was 1-methyl-2-pyrrolidinone, whereas water was used for the others. Fronabarger et al. (1981) evaluated all except the pyrazolato complex. The loose powders were insensitive to the human-body-equivalent electrostatic discharge. For the detonator-loaded condition, electrostatic sensitivity increased in the order 3-NO₂-1,2,4-TrzPCP < 4-NO₂-1,2,3-TrzPCP < 5-NO₂-TzPCP, and ease of growth to detonation followed the same order, with the tetrazolato complex exhibiting greatest spark sensitivity and ease of achieving detonation.

Additional studies are in progress. Johnson et al. (1984) have attempted to synthesize and characterize analogues of CP in which the cobalt atom has been replaced by chromium, rhodium, ruthenium, and iridium. The chromium and rhodium compounds have been satisfactorily prepared and characterized, whereas the others have been shown to consist of product mixtures. Such compounds provide variations in thermal stability, metal-to-ammine bond strength, and possible oxidation states. Replacement of the perchlorate anion by other oxidizing anions and replacement of the cyanotetrazolato ligand by additional trigger groups are being examined. The utilization of tetraamines or polymeric coordination compounds are under consideration. At this stage correlations appear to exist between the electron-withdrawing character of various moieties and the resultant functional properties. Much remains to be done to determine whether chemical "tailoring" can yield materials with tailored explosive performance characteristics.

Acknowledgment

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Registry No. CP, 68147-80-8.

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Fundamental Research on Explosives Program

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The Fundamental Research on Explosives (FRE) program is a multidisciplinary, Laboratory-wide fundamental research effort whose aim is to gain a detailed molecular-level understanding of the energetics of liquid nitric oxide decomposition that supports the phenomenon of detonation in that system. In the FRE program we are interested in the details of the acquisition and maintenance of steady detonation in liquid nitric oxide and in how this steady condition compares to the existing (Chapman-Jouguet) theory of steady detonation.

Introduction

The Fundamental Research on Explosives (FRE) program was initiated as a 5-year program beginning in fiscal year 1982. It was established as a Laboratory-wide, coordinated theoretical and experimental effort aimed at gaining a fundamental understanding of detonation behavior using state-of-the-art techniques not previously applied to explosives. The program represents a new approach in our efforts to understand the fundamental processes of detonation. Initial tasks included choosing a prototype explosive molecule simple enough to allow study of the details of the detonation process both experimentally and theoretically. Liquid nitric oxide (NO) was selected.

Subsequently, a plan of attack evolved that established the following goals: (1) determine the equation-of-state (EOS) properties of liquid NO, (2) explore the chemistry of initiating and detonating liquid NO, and (3) measure detonation properties of liquid NO with sufficient precision to enable a test of current Chapman-Jouguet (CJ) theory. A list of fiscal year 1984-participating FRE team members is presented in Table I.

Overview

A. Detonation Products EOS. The experimental portion of the work on the EOS of the detonation products of liquid NO has been successfully completed (Schott et al., 1985). The experimental data, which was obtained in the pressure range of 10-30 GPa, are compared with theoretical Hugoniot curves in Figure 1. Our newly developed method (Johnson et al., 1984; Shaw et al., 1983) for treating nonspherical potentials of molecular fluids using effective spherical potentials coupled with existing mixing rules was utilized in modeling the EOS. Intermolecular potentials were calculated by using ab initio (Hay et al., 1984) and semiempirical methods (Pack, 1984). The agreement between experimental data and theoretical calculations is excellent. The resulting EOS is adequate for our planned test of CJ theory, but the question of what forms of oxidized nitrogen are actually present as products of detonating NO remains to be answered.

B. Shock Wave Measurements. We have experimentally verified the attainment of chemical equilibrium

Table I. FRE Team Members, Fiscal Year 1984

name	category	contributing activity
S. F. Agnew	spectroscopy	spectroscopy of molecules at high density
N. C. Blais	spectroscopy	studies of clusters of explosive molecules
J. B. Cross	spectroscopy	intermolecular forces
W. C. Davis ^a	hydrodynamics	detonation physics
W. Fickett	TAC ^b	technical advisor, detonation physics
N. R. Greiner	spectroscopy	detonation products' chemistry
P. J. Hay	theory	ab initio intermolecular potentials
B. L. Holian	TAC ^b	technical advisor, theory
J. D. Johnson	theory	thermodynamics of dense molecular fluids
R. L. Mills ^a	hydrodynamics	unreacted NO EOS
D. S. Moore	spectroscopy	laser-based diagnostics of shocked materials
N. S. Nogar	spectroscopy	spectroscopy of highly excited molecules
R. T. Pack ^a	theory	semiempirical intermolecular potentials
T. Rivera	project manager	coordination of research program
R. N. Rogers ^a	consultant	explosives' chemistry
R. R. Ryan	TAC ^b	technical advisor, spectroscopy
S. C. Schmidt	hydrodynamics	laser-based diagnostics of shocked material
D. Schiferl	spectroscopy	spectroscopy of molecules at high density
B. I. Schneider	theory	intermolecular potentials
G. L. Schott	hydrodynamics	shocked-state measurements
L. A. Schwalbe	hydrodynamics	unreacted NO EOS
M. S. Shaw	theory	thermodynamics of dense molecular fluids
J. R. Stine	theory	theoretical chemical dynamics
B. I. Swanson	spectroscopy	spectroscopy of molecules at high density
J. J. Valentini	spectroscopy	spectroscopy of highly excited molecules

^a Los Alamos Fellow. ^b Technical Advisory Committee.

in detonating liquid NO. We were able to do this because the same thermodynamic state is reached by shocking either liquid NO or liquid N₂ + O₂ mixtures to ~21 GPa (Schott, 1984). At lower shock pressures, ~3 GPa, we found that the reactions leading to detonation are ap-