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FULMINATES: A LITERATURE SURVEY

by

Hyman Rosenwasser

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FULMINATES: A LITERATURE SURVEY

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**The Commanding Officer
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Prepared by

**Hyman Rosenwasser
Basic Research Laboratory
Military Department**

SUMMARY

Among the aspects discussed in this survey are the preparation of fulminic acid and its polymerization behavior, as well as its application for the synthesis of compounds such as the isoxazoles. Progress in the synthesis of fulminate salts leads from mercuric fulminate to other metallic fulminates, to complexes, and to organometallic derivatives. Studies dealing with structure, solubility, thermal decomposition, and analysis of fulminates are presented.

CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
	SUMMARY	ii
I	INTRODUCTION	1
II	FULMINIC ACID	2
III	FULMINATES	4
IV	FREE RADICALS	11
	LITERATURE CITED	13

FULMINATES: A LITERATURE SURVEY

I. INTRODUCTION

Although the use of mercury fulminate as a primary explosive has diminished considerably, there has been a recent revival of interest in various aspects of fulminate research. Such studies include the synthesis of organometallic fulminates by Beck (Germany), structure of silver fulminate by K. Singh (India), and explosive characteristics of mercury fulminate by Andreev (Russia). This literature survey is intended to serve as a guide for further research on fulminate compounds. It is anticipated that the relatively recent techniques such as electron spin resonance, nuclear magnetic resonance, and differential thermal analysis will be used on fulminates to provide fundamental information on the structure of explosives and their mechanisms of decomposition.

Among the general references which consider fulminates, particularly the mercury salt, are the books by Davis (1), Cook (2), and Bowden and Yoffe (3, 4). Davis has provided information on the history, commercial manufacture, solubility properties, and analysis of mercury fulminate, along with some treatment of its explosive characteristics, such as dead-pressing, impact sensitivity, explosion temperature, and the minimum charge required for detonation of secondary explosives. Comparative data on explosion temperatures and ability to detonate high explosives are tabulated for other fulminates as well. Cook gives the composition of fuse caps, which contain mercury fulminate, and data on mercury fulminate such as the detonation velocity, time lag in impact initiation, specific rate constant for isothermal decomposition, and computed thermodynamic properties. Bowden and Yoffe (3) present results of studies on initiation of mercury fulminate by friction, by impact, and by adiabatic compression of air. Tabulated data in the subsequent monograph (4) include the compression ignition temperature of mercury fulminate and its ignition by light flashes, heat of formation, activation energy for decomposition, specific heat, hardness, thermal conductivity, and combustion of single crystals.

The report by Tomlinson and Sheffield (5) contains results from impact sensitivity, vacuum stability, and sand test measurements, as well as heats of explosion and combustion for mercury fulminate.

II. FULMINIC ACID

According to Wieland (6), the production of fulminic acid from ethyl alcohol and nitric acid occurs in the sequence $\text{EtOH} \rightarrow \text{MeCHO} \rightarrow \text{HONCHCHO} \rightarrow \text{HONCHCOOH} \rightarrow \text{HONC}(\text{NO}_2)\text{COOH} \rightarrow \text{HONCHNO}_2 \rightarrow \text{HONC}$. Experimental evidence for the final step consisted in the synthesis of methylnitrolic acid which, upon boiling in aqueous solution, yielded fulminic acid, formic acid, and nitrous oxide. Precipitation of silver or mercuric fulminate was obtained upon addition of the metal nitrate to the boiled solution. The use of dilute mineral acids was later shown to convert aminomethylnitrolic acid ($\text{HONC}(\text{NH}_2)\text{NO}$) and aminoformoxime (HOCHNOH) into fulminic acid (7).

The free fulminic acid is unstable, volatile, and highly toxic. It may be extracted with ether after conversion of mercuric fulminate into the sodium salt by sodium amalgam, followed by treatment with sulfuric

acid (8). Hodgkinson (9) described fulminic acid as $\begin{array}{c} \text{HCN} \\ | \\ \text{HOC} = \text{N} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{O}$ and

related its formation to the action of N_2O_3 on ethyl alcohol. Pauling and Hendricks (10) assigned the formula HCNO to fulminic acid, based on potential energy calculations, whereas Lindemann and Wiegrebé (11) preferred the structure $\overset{+}{\text{C}} \equiv \overset{-}{\text{N}}\text{OH}$, and Bergfeld (12) the bicarbon formulation, $\text{H}_2\overset{+}{\text{C}} - \text{NO}$. The isolation of two isomeric hydroxytetrazoles from the reaction of sodium fulminate with hydrazoic acid led Palazzo and Marogna (13) to conclude that in solution there is an equilibrium between CNOH and HCNO .

Instability of fulminic acid is caused by its tendency to polymerize, generally to the trimer, isocyanuric (metafulminuric) acid. Such polymerization takes place quickly, for instance, when weak bases are added to an aqueous solution of HONCHCl (14). Considerable controversy arose over the formula for the trimer, as discussed by Ulpiani (15), who himself favored $\text{NCC}(\text{NOH})\text{C}(\text{OH})(\text{NOH})$. "Beilstein's Handbuch der Organische Chemie" (16) gives the formula as $\text{HC}(\text{NOH})\overset{+}{\text{C}}(\text{NOH})\overset{-}{\text{C}}(\text{NOH})$, that is, isonitroso-

isoxazoloneoxime. Heating the metafulminuric acid with sodium carbonate may yield isofulminuric acid, $\text{O} \begin{array}{c} \diagup \text{N} = \overset{+}{\text{C}} \text{CONH} \\ \diagdown \text{NH} - \text{CO} \end{array} 2$ (14). According to Sennewald and Birckenbach (17), fulminic acid polymerizes in the presence of mineral acids by a second-order reaction, whereby dicarbonyl dioxime is formed as an intermediate and reacts further to produce the trimer and some isocyanilic acid, $(\text{CHON})_x$. The tautomerism of fulminic acid and its method of polymerization have been reviewed by Palazzo (18).

Palazzo and Marogna (19) have described the reaction of an inorganic acid, HX, with an aqueous solution of sodium fulminate as leading to the formation of HXCNO_{Na} which, in the presence of excess acid, liberates XHCNOH, followed by partial dissociation of the formoxime. Substituted formoximes of the type HICNOH, HBrCNOH, and NCSCHNOH were prepared (20). The action of chlorine on fulminic acid, generated *in situ*, at 0° C yields Cl₂CNOH (21, 22). Treatment of mercuric fulminate in sulfuric acid with bromine yielded a mixture of dibromoformoxime and dibromofuroxan, (BrCNO)₂ (23). Cl₃CNO and Br₃CNO were obtained from the respective formoxime by addition of an acid solution of sodium acetate in the presence of the halogen.

Nitrile derivatives have been prepared of 1-phenyl-3-methyl pyrazolone (24), barbituric acid, and thiobarbituric acid (25) by refluxing a mercuric fulminate solution in KCN with the respective compound. Similarly prepared were nitrile derivatives of naphthol and of α-methyl indole (26).

Quillico and Speroni (27) synthesized isoxazole derivatives from fulminic acid, such as by condensation with acetone and acetylene in acid medium to yield α-isopropenylisoxazole, H₂CC(CH₃)CCHCHNO. The isoxazole compound forms by dehydration of the intermediate carbinol (28). With methyl ethyl ketone substituted for acetone in the above reaction, a mixture of isoxazole derivatives, as well as tiglic acid, is obtained (29). Fulminic acid prepared *in situ* from the reaction of sodium fulminate and sulfuric acid was reacted with acetylenic compounds (in the absence of ketones) to give 5-hydroxymethyl-3-isoxazolecarboxaldehyde oxime, HONCHCNO(CH₂OH)CH from HC≡CCH₂OH (30) and ONCHCHCPh from phenylacetylene (31). With diacetylene in methanol, the fulminic acid reaction yields a mixture of α-formyl-α, α'-bisoxazole oxime and α, α'-diformyl-α, α'-bisoxazole dioxime (32). The action of fulminic acid solutions on ethylenic compounds also leads to isoxazoles, such as in the preparation of 5-acetoxyisoxazole from CH₂=CHOAc (33).

From triphenylmethyl chloride and silver fulminate, in absolute benzene, was obtained triphenylmethylnitrile oxide, Ph₃CCNO (34). The infrared spectra of some nitril oxides have been measured by Califano and others. The RCNO compounds thus studied were 2,4,6-trimethylbenzotrile oxide, 2,3,5,6-tetramethylbenzotrile oxide, 4-chlorobenzotrile oxide (35), and trimethylacetotrile oxide (36). Dicyanbis(N-oxide), ONCCNO, was prepared by Grundmann (37). Several aliphatic nitrile oxides, which dimerize to furoxans, were synthesized by Zinner and Günther (38) by dehydrohalogenation from hydroxamic chlorides. Dehydrogenation with alkali hypobromite of alkali salts of oximes yielded stable

aromatic nitrile oxides (39), which rearranged to isocyanates upon heat treatment.

III. FULMINATES

1. Synthesis. The preparation of mercuric fulminate, by the addition to ethyl alcohol of a solution of mercury in nitric acid, was described by Howard in 1800. In 1802, silver fulminate was obtained by Brugnatelli by the addition of alcohol and then nitric acid to powdered silver nitrate (1). Methods for preparing colloidal aggregates (40) and small crystals (41) of silver fulminate are described by Taylor and others. The cadmium, thal- lous, and cuprous salts of fulminic acid were obtained by reaction of either mercuric or silver fulminate with the amalgam of the particular metal, in dry methanol and a hydrogen atmosphere, the products being precipitated out with ether (42, 43). Cd fulminate is stable when dry but readily decom- poses in water and is sensitive to heat or shock. The Cu(I) salt is insol- ible in water and also highly explosive. Thallous fulminate is sensitive to moisture and light and susceptible to heat and shock but does not explode violently. Langhans (44) reviewed the preparation of fulminates (and also noted the effect of moist mercury fulminate upon metals). The fulminates of sodium, potassium, calcium, strontium, and barium were similarly prepared by reaction of the appropriate amalgam with mercuric fulminate, in BaO-distilled methanol (42, 45). Shaking of the reaction medium was continued until Hg was no longer detected with SnCl_2 . Temperatures from -5° to -15° C were used to avoid polymerization. The solutions were filt- ered into cold, dry ether in an oxygen-free atmosphere. The alkaline earth fulminates separated with 1 mole of methanol, which could not be driven off without decomposition of the salts. Both the alkali and the alkaline earth fulminates are unstable to CO_2 and moisture. Rubidium and cesium fulmi- nates were prepared by Hackspill and Schumacher (46), and crystals, prob- ably in the hexagonal system, were formed by evaporation from methanoi solution (47). The dry alkali fulminates detonate easily by friction or tem- perature increase, and the higher the molecular weight the more violent is the detonation. Double salts of the alkali fulminates with mercuric fulmi- nate are even more sensitive.

Complex argentofulminates such as $\text{NH}_4\text{Ag}(\text{CNO})_2$ and $\text{MgAg}(\text{CNO})_2$ were prepared from silver fulminate and the corresponding iodide in ether (45). Neither salt is light-sensitive; the latter detonates violently under certain conditions. Well-crystallized complexes containing 2 moles of pyridine were obtained for the fulminates of Zn, Cu(I), Ag, Cd (and Hg) by shaking mercuric fulminate in pyridine with the respective metal amalgams.

The corresponding Pb complex generally deflagrated during drying in an evacuated desiccator. The alkali and alkaline earth fulminates showed no tendency to form the pyridine complexes. Other fulminato complexes, prepared by Wöhler and Berthmann (48), are $2\text{Hg}(\text{CNO})_2 \cdot \text{Na}_2\text{S}_2\text{O}_3$, $\text{Hg}(\text{CNO})_2 \cdot \text{NaCl}$, $\text{Hg}(\text{CNO})_2 \cdot \text{KBr}$, $\text{Hg}(\text{CNO})_2 \cdot \text{MgCl}_2$, $\text{Zn}(\text{CNO})_2 \cdot 2\text{NH}_3$, $\text{Mn}(\text{CNO})_2 \cdot 2\text{NH}_3$, $\text{Na}_2\text{Ni}(\text{CNO})_4 \cdot 5\text{H}_2\text{O}$ (brown), $\text{K}_5\text{Co}(\text{CNO})_{11} \cdot 22\text{H}_2\text{O}$ (yellow), $\text{Na}_2\text{Pt}(\text{CNO})_4 \cdot 5\text{H}_2\text{O}$ (colorless, red if dehydrated), $\text{CaPt}(\text{CNO})_4 \cdot 5\text{H}_2\text{O}$ (yellow, green if dehydrated), $\text{SrPt}(\text{CNO})_4$ (red), $\text{BaPt}(\text{CNO})_4 \cdot 3\text{H}_2\text{O}$ (colorless, red if dehydrated), $\text{Na}_2\text{Pd}(\text{CNO})_4 \cdot 5\text{H}_2\text{O}$, $\text{NaAu}(\text{CNO})_4$, $\text{NaCu}(\text{CNO})_2$, $\text{SrCu}_2(\text{CNO})_4 \cdot 2\text{H}_2\text{O}$, $\text{CuCu}_2(\text{CNO})_4 \cdot 2\text{H}_2\text{O}$ (green), $\text{Na}_2\text{Cu}(\text{CNO})_3 \cdot 3\text{H}_2\text{O}$, $\text{CaCu}(\text{CNO})_3 \cdot 3\text{H}_2\text{O}$, $\text{SrCu}(\text{CNO})_3 \cdot 6\text{H}_2\text{O}$, and $\text{BaCu}(\text{CNO})_4 \cdot 4\text{H}_2\text{O}$.

Beck (49) synthesized the complex compound $[\text{Cr}(\text{en})_3] [\text{Co}(\text{CNO})_6] \cdot 3\text{H}_2\text{O}$ by exposing a solution of CoSO_4 and NaCNO to light, followed by treatment with $[\text{Cr}(\text{en})_3]^{3+}$ at 0°C . This water-insoluble, yellow compound shows a magnetic moment of 3.98 Bohr magnetons, corresponding to three unpaired electrons. Similar measurements showed the complexes $\text{Na}_2\text{Ni}(\text{CNO})_4 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_4\text{Fe}(\text{CNO})_6 \cdot 18\text{H}_2\text{O}$ to be diamagnetic. Infrared absorption frequencies for these complex salts were also measured. Radiochemical studies (50) showed that reduction of the hexafulminatoferrate(II) ion to the hexacyanoferrate(II) ion took place in alkaline solution without breaking of the complex bond, thus proving that bonding to the Fe atom is through the C atom. Reduction of the tetrafulminatonickel salt with sodium amalgam gave a mixture of $\text{Na}_2\text{Ni}(\text{CN})_4$ and $\text{Na}_4\text{Ni}(\text{CN})_6$. A mixed cyanofulminato, diamagnetic compound with the composition $\text{Na}_4\text{Fe}(\text{CN})_5\text{CNO}$ was prepared by reaction of sodium pentacyanoammine- or aquoferrate(II) with sodium fulminate (51). $\text{Fe}(\text{OH})_2$ reduces cyano-fulminate to the hexacyanoferrate(II) ion. Infrared data for the hydrate $\text{Na}_4\text{Fe}(\text{CN})_5\text{CNO} \cdot 3/2\text{H}_2\text{O}$ is compared with that for other prussiate-type salts.

From the reaction of transition metal sulfates with sodium fulminate and either o-phenanthroline or α, α' -bipyridyl, Beck and Schuierer (52) obtained $\text{Fe}(\text{phen})_2(\text{CNO})_2$ and its monohydrate (violet), $\text{Fe}(\text{bipyridyl})_2(\text{CNO})_2 \cdot 1/2\text{H}_2\text{O}$ (black), $[\text{Ni}(\text{phen})_3][\text{Ni}(\text{CNO})_4] \cdot \text{H}_2\text{O}$ and the corresponding methanolate and bipyridyl salt (pink), $\text{Mn}(\text{phen})_2(\text{CNO})_2 \cdot 1/3\text{H}_2\text{O}$ and the anhydrous bipyridyl complex (yellow), $[\text{Co}(\text{phen})_3]_3[\text{Co}(\text{CNO})_6]_2 \cdot 10\text{H}_2\text{O}$ and the dihydrate (yellow), $[\text{Co}(\text{bipyridyl})_3]_3[\text{Co}(\text{CNO})_6]_2 \cdot 9\text{H}_2\text{O}$ (brown), and $\text{Co}(\text{phen})_2(\text{CNO})_3 \cdot \text{H}_2\text{O}$ (yellow). Infrared spectral data and conductivities in dimethylsulfoxide were recorded for most of these compounds. The anhydrous $\text{Fe}(\text{phen})_2(\text{CNO})_2$ and the corresponding bipyridyl complex can add 1 mole of BF_3 per mole of fulminate ligand to form yellowish-brown adducts (53).

Triorganometallic fulminates of the Group IV elements have been synthesized by Beck and Schuierer (54). Ph_3SiCNO was prepared from the triphenylsilyl chloride by metathesis with sodium fulminate, and Ph_3GeCNO from the corresponding bromide. A $d\pi - p\pi$ bond between Si and CNO is indicated for the Ph_3SiCNO compound. Ph_3SnCNO was obtained from reaction of the corresponding chloride with potassium fulminate, and Ph_3PbCNO from the organometallic hydroxide and sodium fulminate. The reaction between tripropyllead hydroxide and potassium fulminate yielded $(n - \text{Pr})_3\text{PbCNO}$, which is sensitive to heat and friction. Melting points, solubility characteristics, and infrared absorption frequencies are tabulated for these compounds. Organomercury and organothallium fulminates of the type RHgCNO and RTlCNO were also prepared (55). Thus, $\text{PtCH}_2\text{HgCNO}$ was obtained from benzylmercury chloride and KCNO . PhHgCNO was prepared from diphenylmercury, or phenylmagnesium bromide, and mercuric fulminate. Similarly obtained were *o*-tolylmercury and 1-naphthylmercury fulminates from the respective arylmagnesium bromides. Ph_2TlCNO and Me_2TlCNO were prepared from the corresponding organothallium fluorides and NaCNO solution. The ionic dimethylthallium fulminate is explosive, whereas the arylmetal fulminates are not.

Phosphine-containing fulminato complexes of the type $(\text{R}_3\text{P})_2\text{M}(\text{CNO})_2$ have been made, where R = Ethyl, Naphthyl, Phenyl and M = Ni, Pd, Pt (56). The general method of preparation was to react the tetrafulminate complex of the metal with the tertiary phosphine. Compounds thus synthesized were (a) $(\text{Et}_3\text{P})_2\text{Ni}(\text{CNO})_2$ (yellow), (b) $(\text{Et}_3\text{P})_2\text{Pd}(\text{CNO})_2$ (colorless), (c) $(\text{Et}_3\text{P})_2\text{Pt}(\text{CNO})_2$, (d) $(\text{Naph}_3\text{P})_2\text{Pd}(\text{CNO})_2$, (e) $(\text{Naph}_3\text{P})_2\text{Pt}(\text{CNO})_2$, (f) $(\text{Ph}_3\text{P})_2\text{Pd}(\text{CNO})_2$, (g) $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CNO})_2$, (h) $\text{Ph}_2\text{PCH}_2\text{-CH}_2\text{PPh}_2\text{Pd}(\text{CNO})_2$, (i) $\text{Ph}_2\text{PCH}_2\text{-CH}_2\text{PPh}_2\text{Pt}(\text{CNO})_2$, and (j) $(\text{Ph}_3\text{P})_2\text{Hg}(\text{CNO})_2$. Thermal stability increases from (a) to (c). All these tetracoordinated bisphosphine metal fulminates are diamagnetic and have planar structures (57). Complexes (a) through (g) have a trans configuration as indicated by low dipole moments, whereas (h) and (i) have the fulminate ligands in cis positions, since two NO bands are observed in the infrared spectra. Observed stretching frequencies for $(\text{Et}_3\text{P})_2\text{PtHCNO}$, and the corresponding deuteride, indicate a large trans effect for the fulminate ion.

2. Structure. Based on iodometric titration data, van Leent (58) considered mercuric fulminate as an isocarbonitrile of mercury peroxide. Infrared spectral data for Hg, Ag, and Pb fulminates were obtained by Singh (59). From ultraviolet absorption spectra and quantum mechanical calculations, it was concluded that $-\bar{\text{O}}-\text{N}\equiv\text{C}$ is the most probable structure for the fulminate ion. Beck (60) measured the infrared absorption frequencies for sodium and potassium fulminates and calculated the force constants for the linear CNO^- ion.

Photomicrographs of mercuric fulminate crystals have been published by Olsen (61) and Langhans (62). Miles (63) crystallized mercuric fulminate from a solvent mixture of ammonia, water, and ethanol. The diamond-shaped, orthorhombic crystals had a density of 4.307. Axial ratios for a:b:c were 0.712:1:1.353; observed angles for (010):(111) and (100):(111) were $57^{\circ}48'$ and $41^{\circ}30'$, respectively. Laue patterns by Sekiguchi (64) suggested a variant structure of the lattice, possibly related to morphological variations in the rhombic angle. By maintaining the temperature of the reaction mixture of Hg, HNO₃, and alcohol between 60° and 90° C, Endo and Mashima (65) recovered rhombic plates of Hg(CNO)₂. However, they claimed that rhombic pyramids of HgCNO formed if the mixture was maintained at 45° to 55° C. Singh (66) reported that the latter procedure produces a mixture of mercuric fulminate and mercury. Kast and Selle (67) crystallized mercuric fulminate from KCN and from boiled water. Analysis for mercury content indicated the absence of water of crystallization. Nagayama and Mizushima (68) obtained different crystal habits of mercuric fulminate by varying the rate of crystallization from solutions. Crystals obtained from hot water were the most sensitive. Otto (69) discounted previous claims (70) that mercuric fulminate belonged to the monoclinic system.

Suzuki (71) obtained cell dimensions of $a = 7.71$, $b = 5.48$, and $c = 10.43\text{Å}$ from the structure determination of single crystal mercuric fulminate. The unit cell contains four molecules, and the space group is D_{2h}^{15} . The most probable configuration has the cylindrical axis of each fulminate ion oriented along the c-axis. The structure of silver fulminate was determined by Singh (72) on needle-shaped crystals obtained out of ammonium acetate solution. The orthorhombic crystals have cell constants of $a = 6.04$, $b = 3.88$, and $c = 11.20\text{Å}$, with the space group $Imca$ (probable), $Z = 4$, and d (calcd) = 3.936. A refractive index of 1.630 was obtained along the needle a-axis and 1.831 along the b-axis. According to Pandey (73), the type of diffraction pattern obtained for silver fulminate is dependent upon the pH of the crystal-growing medium. In the absence of acetic acid, only powder patterns were obtained for the crystals. Evans and Yoffe (74) have provided refractive index curves in the 4500 to 7000 Å region for silver fulminate.

3. Decomposition. Peter (75) observed that silver fulminate kept under water for 40 years in a stoppered bottle was colored gray but retained its composition and explosive properties. Singh and Palkar (76) studied the isothermal decomposition of silver fulminate at various temperatures from 190° to 210° C. Beyond these temperatures, the reaction tends to build up explosively. First-order kinetics was obtained during the initial decay, followed by an acceleratory stage with an activation energy of 28.62 kilocalories per mole. Based on absorption edge and dielectric constant data,

it is suggested that the rate-determining step involves electron transfer from the top of the fulminate band to the top of the Fermi level of the silver nuclei. X-ray patterns of partially decomposed AgCNO crystals showed rings of randomly oriented Ag crystallites superimposed on the original diffraction spots.

Farmer (77) noted an induction period in the prolonged thermal decomposition of brown and white mercuric fulminates, in vacuo, at 80° C. This period was followed by gas evolution, which increased rapidly to a constant velocity until the gas ceased, leaving an inert residue. (Studies were also made of mixtures of mercuric fulminate with metals, metal oxides, metal carbonates, and organic nitrogen bases, respectively.) Langhans (78) considered the brown, insensitive decomposition product (pyrofulmin) to be a mixture of mercuric oxycyanide and oxide. Pyrofulmin yields were determined for various heat treatments of the fulminate. According to Singh (55), infrared spectra of pyrofulmin indicate the presence of NCN and CN groups. Kast and Haid (79) showed that mixtures of mercuric fulminate with $KClO_3$ decomposed slowly at 155° to 160° and rapidly at 175° to 180° and exploded at 215° C. The critical pressures required for spontaneous ignition of mercuric fulminate were determined by Patry and Lafitte (80). Garner and Hailes (81) determined that decomposition in vacuo passed into detonation at 105° to 115° C during the acceleratory period. Reaction kinetics for the mechanism have been discussed (82). Carl (83) has postulated that the decomposition of mercuric fulminate is a catalyzed reaction and this catalysis reduces initiating effectiveness. Vaughan and Phillips (84) presented evidence for self-heating and the formation of a nonvolatile catalyst during the induction period preceding explosion. For thermal decomposition in vacuo at temperatures between 70° and 100° C, the gases evolved were 93 percent CO_2 , 5 percent N_2 , and some N_2O and CO , with an activation energy of 25.4 kilocalories per mole for the process. Bartlett, Tompkins, and Young (85) showed that gas evolution during decomposition at 100° C was altered if the fulminate crystals were aged, irradiated, or crushed prior to heat treatment. The results were related to behavior at subgrain boundaries. Microscopic observations by Singh (86) indicated preferential decomposition along (010) and (100) planes and along surface growth marks of mercuric fulminate crystals. Decomposition was related to dislocation pileup, as well as to gas evolution and pyrofulmin from fulminate radicals. At 170° C, the critical thickness for surviving explosive decomposition was 22 ± 3 microns, equivalent to the theoretically derived "hot spot." Yamamoto (87) showed the collapse of mercuric fulminate crystals and breakup of crystals into fragments by application of electron microscopy. Sekiguchi and Oshimi (88) followed the thermal decomposition of mercuric fulminate to the cyanate by means of

Laue patterns. Beck (60) also observed cyanate ion in the careful thermal decomposition of Na and K fulminates. Hackspill and Schumacher (46) heated Rb and Cs fulminates in vacuo at 200° C. The decomposition was analyzed to be $3 \text{ CNOM} \rightarrow 2\text{CO} + 1/2(\text{CN})_2 + \text{M}_2\text{O} + \text{M} + \text{N}_2$. Yamamoto (89) used DTA and TGA to compare the thermal decompositions of lead trinitroresorcinolate and mercuric fulminate.

Exposure of mercuric fulminate to light at ordinary temperatures causes slow decomposition (77). Long exposure to ultraviolet light or partial decomposition at 123° C is reported to yield a black, more inflammable substance than mercuric fulminate itself (80). Borocco (90) noted that the color of ultraviolet-irradiated mercuric fulminate changes from yellow to brown with increasing dosage. The effects were attributed to slight decomposition of the fulminate to Hg, CO, and N₂. The volume of gas evolved by mercuric fulminate upon exposure to gamma rays has been measured (91).

Langhans (92) observed that the explosion of dry mercuric fulminate could detonate a sample covered by water. Data on the thermal and explosive characteristics of mercuric fulminate, such as heat of formation, decomposition temperature, heat of combustion, rate of detonation, and volume of gas produced, have been listed by Muraour (93) and used for a theoretical treatment of explosive reactions. More recent studies on explosive characteristics of the fulminates are as follows: Yamamoto (94) determined that the ignition point of a Hg(CNO)₂ - KClO₃ mixture was higher than that of Hg(CNO)₂ alone. Bowden and Williams (95) compared the rate of propagation of sodium fulminate, ignited by a hot wire, with those of the heavy metal fulminates (Hg, Cu, Ag, Tl, Cd) and related the probability of explosion to covalent character. Burning speed has been correlated with the physical structure of mercuric fulminate (96), and explosive properties have been tabulated for Na, Tl, and Ag fulminates (74). The combustion and explosion of single crystals of mercuric fulminate, ignited by a platinum wire or cyanuric triazide, have been photographed with a high-speed camera (97, 98).

Studies of impact sensitivity of mercuric fulminate have been made by Murgai and Ray (99) and by Andreev and Terebilina (100). Other recent data for mercuric fulminate include studies on heat of explosion (101), burning to detonation (102), effective combustion temperature (103), minimum charge for detonation (104), ignition delay and intensity (105), combustion gases (106), reaction and lag times (107), detonation velocity obtained using an image converter (108), and range-energy relations for protons and alpha particles (109). For silver fulminate, a deflagration temperature (169° to 175° C) was obtained (110).

4. Solubility and Analysis. Inorganic solvents for mercuric fulminate are KCN, NH_4OH , $\text{Na}_2\text{S}_2\text{O}_3$, and KI, whereas organic solvents are pyridine and methylamines (62). The KCN solutions are unstable and turn brown to red-violet. A crystalline double salt of the fulminate with NH_4SCN can be formed from this solution. Solutions of mercuric fulminate in the methylamines, aniline, paratoluidine, or naphthylamine decompose on standing. Pyridine is a true solvent and the fulminate precipitates on dilution. Mercuric fulminate is slightly soluble in ethyl alcohol and in acetone but is insoluble in benzene, chloroform, or glycerol. A 50-gram-per-liter cold aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_3$ is reportedly a good solvent (111). Monoethanolamine mixed with an equal volume of concentrated NH_4OH dissolves fulminates of mercury and silver without spontaneous decomposition. This solvent mixture has been used for crystallization and purification (112). The fulminates can be precipitated out by acetic acid. Wolf (113) has precipitated fine plates of mercuric fulminate by adding a solution of the fulminate in $\text{Na}_2\text{S}_2\text{O}_3$ to a solution of KCNS. Langhans (78) reported that solutions of mercuric fulminate in $\text{Na}_2\text{S}_2\text{O}_3$ deposit HgS on standing. The fulminate dissolves in nitric acid with decomposition and detonates in concentrated sulfuric acid. Studies were also made with HF and aqua regia as solvents. Cold Na_2SO_3 solution reacts with mercuric fulminate to form double salts such as $\text{Na}_2\text{SO}_3 \cdot \text{HgSO}_3$, whereas NaHSO_3 reacts to give a precipitate of Hg and HgS.

A standard method for determining fulminate content is by HCl titration of the alkalinity resulting from dissolution of the fulminate in excess $\text{Na}_2\text{S}_2\text{O}_3$ solution (114). The fulminate content can also be determined by titration of excess thiosulfate with iodine solution and starch indicator (115). These titrations must be performed rapidly after addition of the thiosulfate. The presence of KI helps to retard the rate of decomposition and thus reduces somewhat the influence of time on the titration. H_3BO_3 has been used as a substitute for KI (116). Another volumetric method which has been used involves addition of iron alum solution to mercuric fulminate in cold HCl and subsequent titration with KMnO_4 solution (117). Analyses of mercuric fulminate have also been made electrolytically (118) and polarographically (119).

The manufactured mercuric fulminate generally contains explosive mercuric oxalate. This can be analyzed for by dissolving the fulminate in NH_4OH , reprecipitating with acetic acid, and adding CaCl_2 to the filtrate (120). Analysis of detonator mixtures is described by Nicolardot and Boudet (121) and includes the determination of KClO_3 , KNO_3 , and Sb_2S_3 . According to Wöhler and Berthmann (122), the commercial white mercuric fulminate is 98- to 99-percent pure. The brown-colored product, of equal

purity, is caused by fulminic acid polymerization, and the gray-colored fulminate contains reduced mercury. The free-mercury content in mercuric fulminate depends on the amount of mercury originally dissolved in nitric acid for the preparation of the explosive (123).

When H_2S acts on a suspension of mercuric fulminate in water, the filtrate gives the reaction of $HSCN$ (124). The formation of $HSCN$ was also detected when Sb_2S_3 , Sb_2S_5 , AsS , As_2S_3 , ZnS , FeS , or FeS_2 was used in place of H_2S (125). Prussian blue formed when the FeS reaction mixture with mercuric fulminate was treated with concentrated HCl . A solution of Na_3SbS_4 (Schlippe's salt) gives a yellow precipitate with solid mercuric fulminate, followed by changes in color from green to black (126). With phenylhydrazine, solid mercuric fulminate turns olive green before changing to gray (127). Primer pellets containing $Hg(CNO)_2$ and $KClO_3$ turned blue-green when covered with concentrated HCl and blue when covered with hypobromite (128). Fulminates react with ferricyanides, in neutral or alkaline solutions, to provide a rose-red color suitable for endpoint determination (129). The absorption spectrum of the complex formed by horse methemoglobin with sodium fulminate has been obtained (130).

IV. FREE RADICALS

The ultraviolet absorption spectrum obtained after flash photolysis of a fulminic acid-argon mixture was attributed to the $CN\cdot$ radical by McGrath and Morrow (131). Because of intensity alternation and triplet splitting near 3920\AA , Herzberg and Travis (132) considered the flash photolysis of fulminic acid as leading to the formation of the NCN radical.

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13 ABSTRACT Among the aspects discussed in this survey are the preparation of fulminic acid and its polymerization behavior, as well as its application for the synthesis of compounds such as the isoxazoles. Progress in the synthesis of fulminate salts leads from mercuric fulminate to other metallic fulminates, to complexes, and to organometallic derivatives. Studies dealing with structure, solubility, thermal decomposition, and analysis of fulminates are presented.		

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