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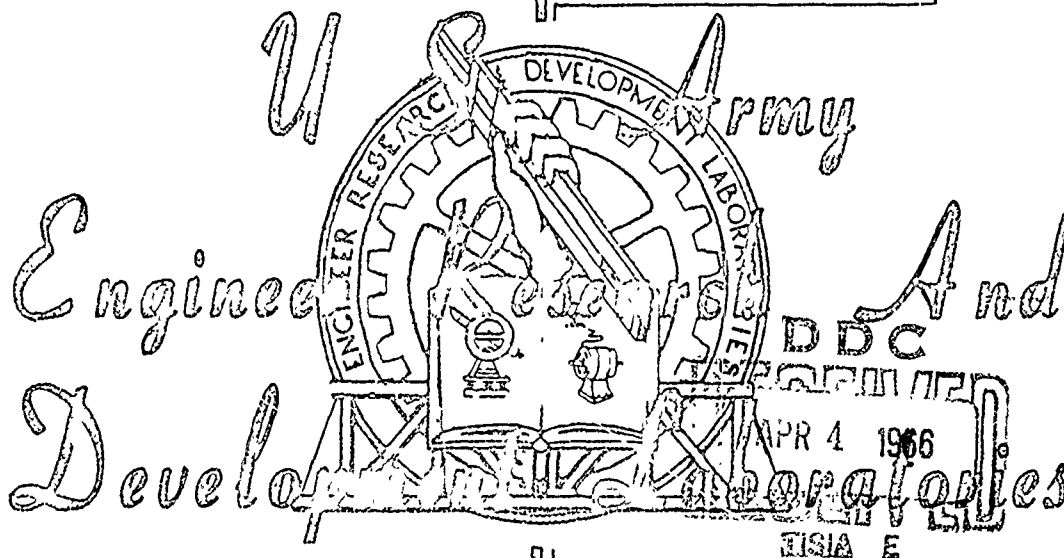
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Authors: Lothar Wöhler and F. Martin

NEW FULMINATES AND
AZIDES

Art. 88 from "Chemische Berichte"
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NEW FULMINATES AND
AZIDES

Lothar Wöhler and F. Martin

The Chemistry Institutes of the Karlsruhe
and Darmstadt Schools
of Technology.

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NEW FULMINATES AND AZIDES

/586

"Chemische Berichte" 1917 Art. 88.

I. Fulminates

The keystone in the investigations on the composition of fulminic acid was formed by the determination of molecular weight in the anhydrous sodium salt of fulminic acid. Through measurement of freezing-point lowering and conductivity of its aqueous solution, this led to the formula CMONa (ref.1). The preparation of sodium fulminate was successful through the simple process of permitting sodium amalgam to act on fulminating mercury under alcohol.

/587

In addition to mercury and silver fulminate and the anhydrous sodium salt --which had already been obtained by Ehrenberg in hydrous and consequently easily decomposing state --, simple salts of fulminic acid have so far not become known although scarcely any other compound has occupied as much as fulminic acid every decade of the last chemical century (ref.2). With double conversion in aqueous solution, there are produced, due to the weak character of fulminic acid, frequently complexes such as the potassium silver fulminate of Liebig or basic salts by hydrolytic dissociation. The complicated fulminating-mercury process (ref.3) for preparation from alcohol and nitric acid can only be applied to the silver salt but fails already with the copper salt because here only insoluble salts are stable, but, due to the oxidation process, only the higher oxidation stages originate which are generally soluble and are therefore subject to further decomposition.

Even so, fulminic acid offers an opportunity, like hydrazoic acid, by its established simplicity and through knowledge of the entire series of its salts to investigate the influence of the degree of affinity of the metallic bases --derived from the electrochemical series -- on explosive properties, on sensitivity to impact and temperature increase, on generation of heat, on detonation speed, and on initiating power. However, the interrelations of these physical constants are in turn of the greatest importance for the chemistry of explosives just like, on the other hand, a comparison of these constants in the series of salts of the fulminates with those of the series of the salts of the azides is highly pertinent.

We are now successful in applying the method utilized for the preparation of sodium fulminate by chemical conversion

of fulminating mercury or fulminating silver, through less noble metals in the form of amalgams, to the preparation of a large number of new simple and anhydrous fulminates. Due to the risk of hydrolytic dissociation, this must not be done, any more than for anhydrous sodium fulminate, in an aqueous solution -- with the exception of the entirely insoluble copper fulminate -- because free fulminic acid tends greatly to polymerization and the formation of polymeric salts. Conversion further furnishes the more noble metal from the fulminating mercury or silver frequently in an inconveniently fine distribution which considerably interferes with the separation of the new fulminate. When employing sodium amalgam and fulminating mercury under alcohol, this difficulty could be overcome but necessitated in other salts a new solvent for the fulminate created for which dry methyl alcohol has proved itself since the fulminate can then be precipitated with ether. We were thus successful in obtaining the fulminates of potassium and the alkaline earths together with that of manganese (on which we shall report later) and also those of copper, thallium and cadmium which, in the chemistry of explosives, are related by their properties to fulminating mercury and silver as well as to the azides of the heavy metals and which will therefore be described here in connection with research on the chemistry of explosives on which we are reporting simultaneously elsewhere (ref.4).

Experimental Procedure

The conversion with amalgams takes place in a rubber-stoppered flask under mechanical shaking with not more than 1-2 g mercury and/or silver fulminate and in dry dryhydrogen as does filtration and washing with ether. Drying was carried out under vacuum over calcium chloride in addition to phosphorus pentoxide. It is understood that the greatest care must be exercised in experiments with these highly explosive substances. In order to avoid local injury from explosion, it is necessary to work with long-handled tools and with protective glasses and face mask. These substances should never be stored in glass-stoppered flasks because the dust particles of some of them detonate already when inserting the stopper and thus ignite the entire mass in the vessel.

Fulminating mercury was prepared by pouring a solution of 50 g of metal in 600 g of nitric acid (1.4) with the addition (for "bleaching" as reported earlier) of 0.6 g each of copper and hydrochloric acid (1.18) in 600 ccm alcohol (95 %). This was purified by dissolution in potassium cyanide and reprecipitation under ice cold with nitric acid. Silver fulminate was

obtained and utilized directly from 5 g of metal dissolved in 155 g nitric acid (1.3) through pouring into 150 ccm alcohol (95%).

The relatively low heat of decomposition under vacuum of the fulminates and azides was measured in a small calorimeter whose walls were lined with glass wool as protection against the metal projectiles from detonation.

1. Cadmium Fulminate

/589

The required amalgam was obtained in 6 hours from concentrated cadmium-sulphate solution over about 50 g of mercury as cathode in a breaker with 0.8 A, i.e. was about 20-%, and was repeatedly washed with water and subsequently with methyl alcohol and finally with some of the latter distilled over barium oxide, (with a high cover of glass pearls and wool because the distillate is otherwise difficult to obtain free from baryte).

2 g of fulminating mercury with the addition of 30 ccm of anhydrous methyl alcohol under ice cold were shaken with the amalgam for 25 min until a test of the solution passed through hardened filter with stannous chloride no longer showed a reaction to mercury. The alcoholic solution of the fulminate becomes, without cooling, rapidly yellow through polymerization and the dry residue even more so after evaporation of the alcohol. Filtering was done in a hydrogen stream into anhydrous ether and further washing was made with the latter. The completely white fulminate was dried under vacuum. It subsequently still contains 2% methyl alcohol which is not easily and still incompletely released only after careful heating for 24 hours under vacuum to 55° over phosphorus pentoxide.

The demonstration of the alcohol is made after distillation of the fulminate solution in water through the addition of aqueous silver-nitrate solution for the purpose of precipitating the fulminate and repeated oxidation of the first distillate with an electrically heated copper spiral to formaldehyde which is recognized by the reddish coloration of phloroglucinol in customary manner.

Electrolytic determination of cadmium cannot be made directly from a potassium-cyanide solution although this method of determining cadmium was found by us to be excellent otherwise because the remaining fulminic acid causes values which are too high due to carbon-containing deposits. Instead, the metal was determined, after repeated evaporation with sulphuric acid and calcining, as sulphate which is also an excel-

lent method of determination. Determination of fulminate was carried out, similar to the Volhard cyanide analysis, with silver nitrate in excess which is determined after filtration with ammonium thiocyanate and ferric potassium sulphate as indicator. However, since silver fulminate dissolves appreciably in water and thus gives fulminate values which are too low, we utilized alcoholic silver nitrate and a fulminate solution in methyl alcohol.

$\text{Cd}(\text{CNO})_2$. Ber. Cd 57.23, CNO 42.77.
Cef. " 56.6, " 42.34.

Subsequently, the fulminate still contained 1% methyl alcohol, probably as crystal alcohol, since the residue of the methyl-alcohol solution was recognized as birefringent under the microscope during evaporation under vacuum.

When kept dry, the white salt is entirely stable, relatively soluble in alcohol, easily soluble in methyl alcohol, and very easily soluble in water but here decomposes easily by hydrolysis and the absorption of carbon dioxide as well as through polymerization of the fulminic acid produced. /590

The heat of decomposition measured in the calorimeter vacuum amounted to a mean of 470 cal (475 and/or 465 cal) for 1 g. We utilized for this approximately 0.25 g. each. Due to the high density in combination with the high heat of detonation, cadmium fulminate as explosive shows a particularly high working density which indicates high shattering power, i.e. high effective density and/or working density per unit time. Actually, we found cadmium fulminate to be a substance with extremely high shattering power. Determination of sensitivity to temperature increase and impact produced approximately the same sensitivity as fulminating mercury (ref.5).

2. Thallium Fulminate

100 g amalgam (10-%) obtained from thallium chips and mercury by direct mixture at room temperature, were shaken in absolute alcohol -- distilled over barium oxide -- with 1-2 g fulminating mercury in a dark glass under hydrogen for 24 hours. Subsequently, the suspension was elutriated from the amalgam in a hydrogen stream, repeatedly washed with absolute alcohol after settling, then liberated from suspended mercury through elutriation, filtered, covered with absolute ether and dried in the vacuum dessicator. The white crystalline product must be protected against moisture because it is easily hydrolyzed. It turns superficially yellow under light such as is the case for some heavy-metal azides (ref.6), a change which

must probably be ascribed as with them to the deposition of finely distributed metal in sunlight but is so minor that composition and specifically explosive properties are changed no more than for the azides. Even small impurities of finely distributed mercury have no influence on the former.

Determination of thallium as oxide after its oxidation produces values which are too low and was therefore made with the iodide (ref. 7). The fulminate is dissolved with diluted sulphuric acid and the accompanying insoluble quicksilver filtered out and weighed; after accurate neutralization of the solution by one-fourth of its volume of 5-% potassium iodide solution, the iodide is precipitated, filtered and air-dried. /591
The principal amount is again dried at 100° in a porcelain crucible and then weighed; the small residue on the filter is dissolved in 2/1-n nitric acid, again precipitated with hydrogen iodide, evaporated and treated exactly as the principal amount.

For volumetric determination of fulminate, with silver nitrate, of the thallium fulminate insoluble in alcohol, it was initially converted, by shaking (30 min) with 7-10 ccm of 5-% zinc amalgam (obtained from the metals by heating) per 0.5 g suspended fulminate under 100 cc of absolute methyl alcohol in a small volumetric flask into dissolved zinc fulminate. 25 ccm alcoholic 1/10-silver nitrate solution, completed to 100 ccm and 50 ccm of the filtrate were titrated with a 1/10-solution of ammonium thiocyanate and iron solution:

Tl CNO.	Ber.	Tl 82.92,	CNO 17.08.
Gef.	"	82.5, 82.7,	" 16.90.

Heat of explosion is only 223 cal/g but temperature and impact sensitivity is greater than that of fulminating mercury and cadmium and is the largest of all the fulminates with which we are presently familiar. Moreover, nitric acid already initiates explosion. In spite of its particularly high density and sensitivity, thallium fulminate has only minor working density because of the low heat of detonation and relatively low generation of gas and also shows only rather low shattering power (which is measured in practice by the initiating action on explosives) so that we require, under the same conditions, e.g. for detonation of picric acid, 10 times as much as we need of cadmium fulminate or fulminating silver and 20 times as much as lead azide.

3. Cuprofulminate

Cuprofulminate is almost no subject to hydrolytic dissociation because of its insolubility. Its preparation is therefore made by prolonged shaking -- in water and under hydrogen -- of 2 g of suspended silver fulminate with 12-20 ccm of plastic copper amalgam obtained by electrolysis from concentrated sulphate solution on a mercury cathode. Conversion is terminated when the solution of the deposit in sulphuric acid is free of mercury salt after filtration. In order to reduce impurity of the fulminate through finely distributed colloidal mercury which will otherwise color the entire liquid dark brown, we add 2 drops of 2/1-n sulphuric acid before shaking. As protection against oxidation, we wash under hydrogen first with water, then with alcohol and with anhydrous ether and dry under vacuum to constancy.

For determination of copper, we dissolve in cold sulphuric acid and mix with ammonia in order to be able to filter out and weigh admixed metallic mercury which easily amounts to 1% and subsequently boil down with sulphuric acid until the fulminic acid is determined, exactly as for thallium fulminate, after its conversion into soluble zinc fulminate because the cuprous salt reduces directly added silver nitrate to metal. /592

CuCNO.Ber.Cu 60.21, CNO 39.79.
Gef. " 60.0, CO.1, 59.8 " 38.9, 39.8.

Cuprofulminate is very light gray shading slightly into green-- perhaps even white as chloride if it is not influenced by light -- and is stable when kept dry but oxidizes easily in moist air.

Heat of detonation is 508 cal/g. Sensitivity to temperature increase is approximately that of fulminating mercury and cadmium but is less sensitive to impact than the latter. Its density is lower than that of the other heavy-metal fulminates and its working density consequently only slightly higher than that of the thallium salt; its shattering power is appreciably greater, however, and is only slightly below that of cadmium fulminate.

II. Azides

Normal simple and anhydrous azides of the ammonium sulphides have not yet become known. For reasons stated above, however, it is highly desirable to determine their explosive properties and to complete the series of the heavy-metal oxides with them. Only hydrous nickel azide and potassium double

salts of nickel and cobalt are known (ref. 8). The desired salts easily dissociate under hydrolysis due to their solubility and form insoluble salts (ref. 9). The azides of nickel, cobalt, zinc and manganese could be obtained from the carbonates and in ether solution of hydrazoic acid. They are formed without risk if we gradually introduce 5 g of finely divided sodium azide into the mixture of 100 ccm ether and 2 ccm of concentrated sulphuric acid, shake this and filter out the sodium sulphate. If it is inhaled, the solution causes vertigo and headache and must therefore be handled with caution. The action takes place only very slowly and is terminated even with mechanical shaking only after 3 or 4 days; it is more rapid if dry and very finely divided carbonates, i.e. precipitated cold, are utilized. The end of conversion is recognized by the complete solubility in water of the suspension which is then washed in ether. For zinc azide, an equivalent agent as initial substance is the basic azide made familiar by Curtius and Rissom which must be used for manganese because the simple carbonate here reacts too indifferently. Unfortunately, it is impossible to produce anhydrous azides by this method and subsequent drying furnished only the azide of manganese completely and that of zinc almost anhydrous. /593

Attempts to obtain the normal ferric and chromic azide in similar manner succeeded only imperfectly.

The anhydrous cuprous azide CuN_2 as a further new azide has already been described by us some time ago (ref. 10).

The determination of the hydrazoic acid was made according to Curtius and Rissom by distillation with sulphuric acid and titration of a lye of known content; that of the metals in the distillation residue by electrolysis or gravimetry. Calculation covers the anhydrous sum of the two components, that of the water the substance utilized.

1. Nickel Azide

NiN_6 . Ber. Ni 41.07, N 58.98.
Gef. " 41.3, 41.0 " 57.71, 59.0.

The grainy green powder obtained from ether dissolves easily in water but immediately precipitates in green flakes due to hydrolysis.

It attracts moisture. The bound water -- corresponding to slightly more than 1 mol of reaction water (13%) -- is retained very strongly, partially even after standing for seven

ral weeks under vacuum alongside phosphorus pentoxide. However, nitrogen is dissociated with measurable speed already at 60° so that it cannot be obtained entirely anhydrous without decomposition.

Nickel azide is especially sensitive to friction. Even slight pressure or rubbing between metal and glass leads to very violent explosion. Preparation and testing therefore require extremely great caution.

2. Cobalt Azide

CoN₆. Ber. Co 41.20, N 58.80
Gef. " 41.36, 41.39, " 58.64, 58.5.

In addition to the reddish brown powder of small rounded crystals of the normal hydrous azide, there originates in ether a red-brown solution (probably an ether - soluble complex cobalt-hydrazoic acid) similar to the cobalt-hydrocyanic acids. Accordingly, not the white azide but a brown-red variant, a complex silver salt, is precipitated with silver solution from this. The water content and its low tension, the tendency to easy decomposition and solubility of the azide in water, as well as its tendency to hydrolysis, are entirely similar to the respective properties of nickel azide. If possible, it is even more sensitive to friction than the nickel salt and detonates easily even between cardboard. Since it has a very high shattering power, the risk in handling it far exceeds that from silver and lead azides. /594

3. Zinc Azide

ZnN₆. Ber. Zn 43.71, N 56.29, H₂O -
Gef. " 43.68, " 56.34, " 8.25 (after 1-day
drying)
" " 43.63, " 56.36, " 0.71 (after 5-day
drying).

The hydrous, white, and grainy powder consists of long columnoid crystals, is hygroscopic and can be hydrolyzed like nickel and cobalt azide; in the air, it has a smell of free azoimide and forms a basic salt with water but a clear solution and a complex with hydrogen nitride or sodium azide. Upon ignition, zinc azide smolders only like the alkaline-earth azides and detonates only under strong impact.

Azide is formed also of ethereal azoimide and metallic zinc, but there is simultaneously generated through reduction,

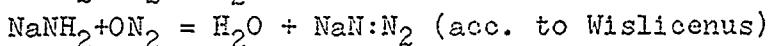
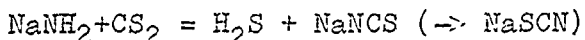
MnN ₅	Ber.	Mn	39.49,	N	60.51,	H ₂ O	-.	
	Gef.	"	39.59,	"	60.42,	"	3.07	(after 2-day drying)
	"	"	39.39,	"	60.61,	"	-	(after 5-day drying)

The grainy crystalline white and normal azide produced from the amorphous basic azide, after brief shaking with the ethereal acid, is hygroscopic and oxidates to black-brown dihydroxide, through hydrolysis which takes place very rapidly under dry heating to 100°. The azide is more sensitive and has a greater shattering power than the zinc salt, without attaining the high sensitivity of the cobalt and nickel azides.

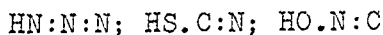
If dry ferric sulphate is shaken in absolute methyl alcohol with sodium azide and the deep dark-red solution evaporated under vacuum alongside of potash and phosphorus pentoxide, we then obtain hygroscopic black-brown flakes, as residue, which hydrolyze under dissolution in water by dissociation of azoimide and therefore produce also a somewhat too low nitrogen content in the analysis. /595

FeN₉. Ber. Fe 30.66, N 69.34.
Gef. " 32.18, 33.17, " 67 83, 66.84.

The characteristic intensive red coloration of the solution so much recalls that of the ferric-thiocyanate complex that it suggests, together with a comparison of the analogous formation of both sodium salts:



the analogy with the 4-member thiocyanic acid or, more correctly, of the isothiocyanic acid. It thus constitutes new support for the Agenli-Thiele assumption of the open constitution of the hydrazoic acid and at the same time thus established a bridge to the similarly constituted fulminic acid with analogous explosive properties:



6. Chromic Azide

From chromic hydroxide precipitated cold, we obtain, by shaking with an alcoholic hydrazoic acid, a dark-green solution and, after evaporation of the latter under vacuum, a black-green hygroscopic mass. Its clear solution becomes turbid only after boiling and, with silver solution, does not produce a white but a green azide so that a complex oxide exists whose content of chromium and nitrogen lies between that of an azido-acid ($\text{Cr}(\text{N}_3)_4$) and a "basic" hydrazoic acid ($\text{Cr}(\text{N}_3)_3\text{OH}\cdot\text{H}$). The substance was not further investigated since it explodes only moderately like ferric azide and thus has no significance for our purposes at the moment.

$[\text{Cr}(\text{N}_3)_3\text{OH}\cdot]$ H. Ber. Cr 29 20, N 70.80.
 $[\text{Cr}(\text{N}_3)_4]$ H. Ber. Cr 27.08, " 72.92.
 Gef. " 27.86, 27.81, N 72.13, 72.19.

For comparison, we list in conclusion the specific detonation heat of the new azides together with those of some known azides as well as those of the known and of the new heavy-metal fulminates which we determined as described.

	cal/g		cal/g
Silver Azide	452	Manganese Azide	676
Lead Azide	364	Calcium Azide	625
Cuprous Azide	582	Strontium Azide	295
Mercurous Azide	266	Silver Fulminate	470
Cadmium Azide	558	Cupro-Fulminate	508
Thallous Azide	232	Thallous Fulminate	223
Nickel Azide	656	Cadmium Fulminate	470
Zinc Azide	360	Mercury Fulminate	397

Summary

/596

1. The previously unknown simple fulminates of cadmium, thallous oxide and cuprous oxide were prepared with the aid of amalgams from silver and mercury fulminate and characterized.

2. From carbonates or basic azides, we newly obtained with ethereal azoimide solution, in addition to the already known hydrous nickel azide, cobalt, zinc and manganese azide whereas ferric and chromic azide were produced as non-uniform complexes.

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