DEPARTMENT OF THE ARMY
U.S. ARMY MOBILITY EQUIPMENT CENTER

CLEARINGHOUSE
FOR FEDERAL SCIENTIFIC AND
TECHNICAL INFORMATION

Hardcopy	Microfiche		
$2.00	$ .50	28 pp	as

ARCHIVE COPY

PROCESSING COPY

[redacted]

AD633399
TT66-61368

Authors: Wöhler Lothar, Weber Al. Berthman A.

T-1826-66

NEW SALTS OF FULMIN~~G~~ic ACID

Two articles

Scientific & Technical Information Division
April, 1966

U.S. Army
Engineer Research And
Development Laboratories

D D C
[illegible]
APR 1 8 1966

FORT BELVOIR, VIRGINIA

OMEFB Label 3

U. S. ARMY ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES
FORT BELVOIR, VIRGINIA

AD-

T-1826 -66

This translation from the German language has been prepared by The Institute of Modern Languages, Inc., Washington, D. C., under Contract No. DA-44-009-AMC-1563(T) in support of ERDL Project No. 1C014501A32B-01 Explosive Research

How to Obtain this Translation

USAERDL personnel may obtain loan copies of this translation from the STINFO Technical Document Center, Building 315 (Vault).

Others

Military agencies and accredited contractors can obtain free copies of this translation from the Defense Documentation Center (DDC), Cameron Station, Alexandria, Virginia 22314.

The general public may purchase only those translations specifically released by USAERDL for sale through the Clearinghouse for Federal Scientific and Technical Information (CFSTI), Sills Building, 5285 Port Royal Road, Springfield, Virginia 22151.

Detailed pricing information may be obtained by contacting directly the above mentioned agency.

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION
USAERDL, FORT BELVOIR, VA. 22060

ERDL T-1826-66

NEW SALTS OF FULMING ACID

Article 437 by Lothar Wohler and Al. Weber
" 438 by Lothar Wohler and A. Berthman

" New Salze der Knallsäure", translated from the " Chemische Berichte", Vol. 62, 2742-2758
Darmstadt, 1929.

NEW SALTS OF FULMINIC ACID

"Chemische Berichte" 1929, Art. 437

/2742

Anhydrous sodium fulminate, CNONa, was prepared long ago (ref. 2) and, from the determination of its molecular weight and conductivity, conclusions were derived on the monomolecular character of fulminic acid, CNOH. By shaking with 10 times the amount of amalgam, we obtained, from 1-1.5 g each of mercury fulminate in very similar manner -- however, with the more solvent dry methyl instead of ethyl alcohol (20 ccm)-- potassium fulminate but the fulminates of calcium, strontium and barium only with a content of crystal alcohol. Magnesium and ammonium salt could not be obtained in the solid state, but only as double salts with silver fulminate.

Methyl alcohol was previously dried by distillation over barium oxide. Shaking was continued until tin (II) chloride showed no further mercury. In order to prevent polymerization, we need to apply low temperature (-5 to -15°) for the alkaline-earth fulminates. Alcohol-soluble difulminates are produced as intermediate products. Filtration takes place in an oxygen-free nitrogen stream into cooled ether which is previously easily dried by shaking with concentrated sulphuric acid. Dry fulminates insoluble in methyl alcohol are more stable to moisture and carbon dioxide than the difulminates. Mercury fulminate is recrystallized by pouring a saturated solution in cold ammonia into cooled diluted acetic acid. The 10-% amalgams were obtained by electrolysis from chlorides and only 5-% amalgam of potassium directly from the components.

Analysis was carried out according to Philip (ref.3) by dissolving the fulminate in excess thiosulphate and retitration of the latter with iodine. The solution becomes alkaline with thiosulphate: one CNO' is only approximately=2OH' so that this last reaction is not usable for analysis. One CNO' is, however, iodometrically exactly = S_2O_3'' . Alkalinity drops under prolonged exposure to thiosulphate whereas iodine consumption increases. However, nothing further is known of the process (ref.4). Within the sense of the following reactions (ref.5)* :

---

* (Note) cf.ref.5.For the complete process, at least 4 $Na_2S_2O_3$ were shown to be necessary and the equation results from this. The intermediate product $Na_2Hg(S_2O_3)2$ is obtained as oil from 5 g $Na_2S_2O_3$ in 10 g of H_2O +2.4 g mercury fulminate with addition of alcohol.

$$\text{Ia.}\quad 2MeCNO+2Na_2S_2O_3+2H_2O=Na_2S_4O_6+2NaOH+2MeOH=C_2N_2$$

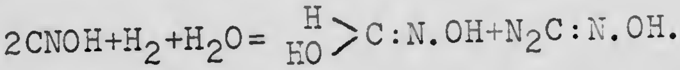
$$\text{Ib.}\quad C_2N_2+2NaOH=CNNa+N\vdots C.ONa,$$

$$\text{2a.}\quad CNNa+Na_2S_2O_3=N\vdots C.SNa+Na_2SO_3 \text{ or 6)}$$

$$\text{2b.}\quad 2CNNa+Na_2S_4O_6+2N_aOH=2NCSNa+Na_2SO_3+Na_2SO_4+H_2O.$$

There originates from tetrathionate in the slow reaction 2-b, under lowering of alkalinity, sulphite consuming iodine. It is further possible to demonstrate S_4O_6'' as stannous salt, SO_3'', SO_4'' $N\vdots CO'$ and $N\vdots CS'$ (ref. 7), in addition to NaOH, in the reaction liquid of sodium fulminate in thiosulphate solution after an additional 12 hours in a well-stoppered flask.

Only hydrocyanic acid can no longer be demonstrated. It is also possible that formohydroxamic acid and formoxime are created under the reducing action of the thiosulphate: /2743



$$2CNOH+H_2+H_2O=\begin{matrix}H\\HO\end{matrix}\!>C:N.OH+N_2C:N.OH.$$

We know (ref.8) that formoxime with P_2O_5 forms hydrocyanic acid. Actually, we observe, under evaporation of the neutralized solution of sodium fulminate and thiosulphate in the dessicator over P_2O_5, a strong smell of hydrocyanic acid.

For preparation, about 0.3 g fulminate are dissolved in 50 ccm of 1/10-$Na_2S_2O_3$. Addition of potassium iodide (Philip) is desirable only with large crystals. We acidify slightly (methyl orange) with sulphuric acid and titrate with 1/10 iodine and starch. 1 ccm 1/10-$Na_2S_2O_3$=0.00421 CNO'.

For mercury fulminate and under rapid titration, the method is exact and also independent of the concentrations. The other insoluble fulminates, silver and cuprofulminate, must previously be converted into an alcoholic zinc-fulminate solution by shaking with zinc amalgam under CH_3. OH and an aliquot part of the solution can be then utilized for titration.

Description of Experiments

Sodium fulminate, CNONa

This was prepared under CH_3 .OH.

0.1773, 0.2932,bzw. 0.2082,0.1245 g Sbst

CNONa.Ber.CNO' 64.62,Na 35.38 Gef.CNO 64.37,64.45,bzw. Na 35.29,35.32.

Legend: bzw = and/or; Ber= theoretical; Gef=experimental; Sbst= substance. Equally applicable to all further specifications given hereafter.

The density determined already earlier is 1.92. The density of silver fulminate has not yet been given in the literature. By pycnometry under benzene, it was determined by us as 4.09; that of mercury fulminate is 4.42 according to Berthollet.

Potassium fulminate, CNOK

Ether should not be used in excess (only about 150 ccm per 20 ccm CHO_3. OH) in order not to precipitate the alcoholate. The fulminate solution rapidly turns yellow through polymerization (ref.9) similar to HCN (ref.10). Alkali determination is made as sulphate under the addition of some HNO_3. The white solid salt is highly deliquescent, i.e. more hydroscopic than the sodium salt, is not soluble in alcohol and acetone, is insoluble in ether and benzol exactly like sodium fulminate and explodes like the latter in the flame with a very sharp detonation. Upon evaporation of the methyl-alcohol solution, we obtain very good crystal needles.

0.1945, 0.2101, 0.1663 bzw. 0.1108,0.2207 g Sbst.
CNOK.Ber.CNO' 51.79,K 48.22. Gef.CNO' 51.37, 51.48, 51.42, K 47.95, 48.08.

Density determined by the suspension method in a mixture of "bromoform" and benzene is 1.80.

The molecular weight of potassium fulminate was found through freezing-point lowering of the water as normal in consideration of the van't Hoff factor $i=I+(n-I)\alpha$ where $\alpha = \lambda/\lambda_\infty$ was determined from conductivity. For vol-mol = 2.5,4,6.5,8, and 12 lt, i= 1.85, 1.88, 1.89, 1.91, 1.93.

CNOK Ber.Mol.-Gew.81.1.Gef.Mol.-Gew.79.5,80.8,79.5,80.0,78.3.

/2744

The difference of molecular conductivity $\lambda_{1024} - \lambda_{32}$ amounts for CN.OK at 15° to only 5.7 (for KCl (15°) 6.4) and at 0° even only 1.0. These figures make clear the hydrolysis of the fulminate which is paralleled by the high conductivity of the lye produced so that the value for α and consequently for i is slightly obscured (German sentence unclear). However, the simple molecular formula CNOK still remains nonambiguous.

Silver fulminate, CNOAg, also produces, in diluted (0.5%) analine solution as solvent (16-20g) the simple molecular weight 144 and 143 instead of 149.9. In contrast to mercury fulminate (ref.11), silver fulminate does not react with aniline and, upon pouring the solution into diluted nitric acid the silver fulminate is again precipitated pure white and without any loss of weight. On the other hand and at higher concentration, silver fulminate precipitates an addition-compound with the aniline which results, at more than 0.5%, in exces - sively high molecular weights; at 2.5% already twice as much if we utilize as molecular freezing-point lowering the experimentally found 58.7 (ref.12), and even higher by 14%, if we utilize the 67.5 derived from the heat of smelting (ref.15).

The addition-compound CNOAg, $2C_6H_5 . NH_2$ is obtained, through saturation at 40° and slow cooling, in 3-4 cm long crystal needles. Upon pouring into ether, we obtain, depending on temperature, a somewhat different aniline content.

a) o.3538, b) 2527 g Sbst. Gef.Ag a) 4132,b)36.16.

CNOAg,$C_6H_5.NH_2$. Ber.Ag. 44.75. CNOAg, $2C_6H_5.NH_2$.Ber.

Ag. 31.10.

Attempts to obtain ammonium fulminate by introducing NH_3 into an ethereal solution of fulminic acid or through double conversion of barium fulminate and $NH_4.NO_3$ in methyl-alcohol solution, resulted only in strongly yellow non-explosive substances which showed an excessive content of NH_4 and, with thiosulphate, no CNO', perhaps due to polymerization. Magnesium fulminate can be obtained in solution by shaking for many hours of 2 g of silver fulminate and $CH_3.OH$ with 5 g of a 60-to 70-% magnesium and copper alloy which is very brittle and therefore can be easily pulverized. However, the turbidity created when the solution flows into ether, becomes viscid-amorphous in spite of cooling with ether and carbon dioxide.

Complex ammonium-silver fulminate $NH_4\ [Ag(CNO)_2]$

From a solution of $NH_4.J$ in $CH_3.OH$ and silver fulminate, there is produced, upon pouring of the filtered solution into ether, the white crystallized salt which dissolves also in $C_2H_5.OH$ and is less explosive than silver fulminate.

0.0946 bzw. 0.1028 g Sbst. Gef.Ag.51.14,NH_4 8.50.

$NH_4\ [Ag(CNO)_2]$. Ber.Ag.51.39,NH_4 8.59.

Complex magnesium-silver fulminate $Mg[Ag(CNO)_2]_2$.

It is obtained analogous with $MgCl_2$ as white water-and alcohol-soluble crystals which detonate violently. It is insensitive to light like the complex ammonium salt whereas pure /2745 silver fulminate is somewhat light-sensitive.

0.1452 g Sbst.Gef.Ag.52.59,Mg 5.86.

$Mg[Ag(CNO)_2]_2$. Ber.Ag 52.88,Mg 5.96

Among the alkaline-earth fulminates, calcium salt is created most quickly whereas barium amalgam requires the longest time of shaking (about 60 min for 1 g mercury fulminate). The crystal alcohol (about 1 mol) cannot be removed by heating without decomposition. The identification of $CH_3.OH$ was made, after precipitation of CNO' with $AgNO_3$ through distillation over redhot copper oxide and demonstration as formaldehyde with phloroglucinol = reddening. Calcium and strontium salt precipitate in ether slightly oily and turn only slowly solid into white, violently detonating incrustations easily soluble in water. Barium fulminate is the most stable and crystallizes well in needles. The solution in $CH_3.OH$ deposits star-like crystals. The analyses are calculated for alcohol free substance, as is generally appropriate for hydrates in order to be independent of the varying content of the latter, so that remaining fulminate and metal must complement each other to 100%. The alcohol content is assumed, however, as residual percentage of fulminate and metal.

Calcium fulminate, $Ca(CNO)_2+CH_3.OH$

I.01172, 0.1602 g Sbst.Gef.Ca 32.53,32.94,CH_3.OH 19.15 18.29 - II.0.2360, 0.2038 g Sbst. Gef. CNO' 67.47,67.06.

$Ca(CNO)_2+CH_3.OH$. Ber.Ca 32.30, CNO'67.70, CH_3.OH 20.59

Strontium fulminate, $Sr(CNO)_2+CH_3.OH$

I.0.1476,II.0.2358 g Sbst. Gef.Sr 51.40,51.52,CH_3.OH 19.76,13.14.-I.0.1777,II.0.2341 g Sbst.Gef.CNO 48.60,48.48.

$Sr(CNO)_2+CH_3.OH$.Ber.Sr.50.45,CNO 49.55,CH_3.OH 16.75.

Barium fulminate, $Ba(CNO)_2+CH_3.OH$

I.0.1667,II.0.1942,III.0.1101 g Sbst.Gef.Ba 63.05,62.10,CH_3.OH 7.35, 10.65, 829.-I.0.1586,II.0.2197,III.0.1372 g Sbst.Gef.CNO 36.95,37.25,37.90.

$Ba(CNO)_2+CH_3.OH$.Ber.Ba.62.05,CNO 37.95,CH_3.OH 12.66.

Upon heating with benzene, it turns yellow and decomposes.

IV.0.1138,0.2280 g Sbst.Gef.Ba 64.80,CNO 35.20.

Solution of zinc fulminate in CH_3.OH deposits upon evaporation only salts rich in zinc and poor in fulminate with about 2.5 mol CH_3.OH which consequently also only deflagrate upon ignition.

Complex pyridine fulminates

Independent of the valence of their metals, the fulminates generally add 2 mol pyridine to well crystallized compounds with weaker deflagration. Those of mercury fulminate and lead fulminate only burn quietly. With amalgam, they can be obtained from mercury fulminate (3 g each dissolved in 21 ccm pyridine) by shaking. Soluble in methyl and ethyl alcohol, insoluble in ether and benzene, they easily decompose through heating also in pyridine solution and therefore release the pyridine partially also to ether in the Soxhlet extraction apparatus, apparently as much more as the atomic volume of the metal is higher; completely with mercury fulminate, less with silver and cadmium, and still less with zinc and copper. They are not very sensitive to moisture and carbon dioxide. /2746

$Zn(CNO)_2$, 2 pyridine

I.0.3873, II.0.2416 g Sebst.Gef.Zn.44.27,43.84,Pyridin 50.98, 51.00.-J.0.2231, II. 0.2707 g Sbst.Gef.CNO 55.73,56.16, .Py 51.50.

$Zn(CNO)_2$, 2Py. Ber. Zn.43.7, CNO56.3, Py 51.5.

Exactly 1 mol pyridine is yielded in ether under shaking. The deflagration of the sandy residue of a similar crystal form then becomes stronger.

0.2846 bzw. 0.2810 g Sbst. Gef. Zn 43.85, Py 34.91,CNO 56.15 $Zn(CNO)_2$,IPy. Ber.Py 34.6

Cu(I)CNO,2pyridine

The amalgam from copper chips easily produced a solution which precipitated the voluminous, well-crystallized complex salt in ether. The remaining fulminate could here be determined only after conversion into zinc-fulminate solution. On exposure to light, the gray-green color turns blue gray. 1 mol pyridine is yielded in ether (b).

a) 0.2549 g Sbst. Gef.Cu 60.15, Py 59.55.- 0.1180 g Sbts. Gef.CNO 39.85.- b) 0.2386 g Sbst. Gef.Cu 60.20,Py 43.00.- 0.2007 g Sbst. Gef.CNO 39.80.

CuCNO,2Py. Ber.Cu 60.2,CNO 39.8, Py 60.0; CuCNO,1Py.Ber. Py 42.8.

AgCNO, I pyridine

This is obtained through saturation of pyridine with silver fulminate at 60° and cooling (a) or by pouring the solution in ether at 18° (b). Strong stirring reduces the pyridine content (c) but it slightly rises (d) at low temperature (-8°). The crystals were dried on filter paper and kept 60 min in the dessicator prior to aralysis.

a) 0.4975 g Sbst. Gef.Ag. 72.05,Py 38.1.-0.1829 g Sbst. Gef.CNO 27.95.-b) 0.2994, 0.1791 g Sbst. Gef.Ag 44.58,44.84, Py 38.06, 37.70.-0.2213 g Sbst. Gef. Ag.72.0.-0.2533 g Sbst. GefCNO 28.0, Py 37.93.-c) 0.3182 g Sbst. Gef.ag 45.25,Py 37.13.-d) 0.2348g Sbst. Gef.Ag 72.08,Py 38.82.-0.1492 g Sbst.Gef. CNO 27.92. AgCNO,I Py .Ber.Ag 47.11, CNO 18.34,Py 34.55;AgCNO. Ber.Ag 71.97, CNO 28.03.

There exists here possibly a crystallized adsorption compound which yields its pyridine, however, very easily to ether in the same way as NH_3 also volatilizes from AgCl,NH_3 at room temperature, whereas AgCl,Py no longer exists at 20° (ref.14)

$Cd(CNO)_2$, 2 pyridine

This is obtained by pouring the voluminous crystal paste produced from pure cadmium fulminate (ref.15) with pyridine into ether, drawing off and drying (a,b). After several hours of shaking, the pyridine is yielded, except for less than 1/3 mol (c), to ether. The finely crystalline yellow /2747 salt deflagrates easily and appears to be already slightly decomposed to judge from the excessive metal content.

a) 0.2488 g Sbst. Gef.Cad 57.25,Py 44.38.-0.2872 g Sbst. Gef. CNO 42.75.-b)0.2204 g Sbst.Gef.C d 57.24,Py 44.58.-0.2373 g Sbst. Gef. CNO 42.76.-c) 0.2234 g Sbst.Gef.Cd. 58.88,Py 12.85.- 0.2393 g Sbst. Gef. CNO 41.12.

$Cd(CNO)_2$,2Py. Ber.Cd. 57.23,CNO 42.77,Py 44.62

$Hg(CNO)_2$, 2 pyridine

The mica-like lustrous flakes obtained upon pouring the pyridine solution of mercury fulminate into ether (a,b) crumble already at room temperature and yield their pyridine completely to ether (c).

a)0.3685 g Sbst.Gef. Hg70.45, Py 33.99.-0.2079 g Sbst. Gef. CNO 29.55.-b)0.2868 g Sbst. Gef. Hg 70.52, Py 35.08.-0.3594 g Sbst. Gef. CNO 2948.-c) 0.20 92 g Sbst. Gef. Hg.69.03 - 0.3138 g Sbst. Gef. CNO 28.97.

$Hg(CNO)_2$, 2Py. Ber. Gh 70.42, CNO 29.58,Py 35.75.

$Pb(CNO)_2$, 2 pyridine(?)

Shaking with lead amalgam under nitrogen until the clear pyridine solution (2 g mercury fulminate + 20 pyridine) no longer contains mercury, forms the brown salt not easily soluble in pyridine which, when decanted from the amalgam sediment, separates insolubly in ether but turns dark brown upon drying and consequently undergoes a chemical change. However, if we previously heat the brown sediment to 30-35° and pour the solution through a glass filter into cooled ether, we then obtain white flakes which turn yellow after some seconds. In the dessicator, the salt regularly deflagrates a few minutes after evacuation which projects the dessicator cover upward and precipitates a fine lustrous lead dust. Only once in 6 experiments was the product obtained dry.

$Pb(CNO)_2$,2Py.Ber.Pb 36.88,CNO 14.97,Py48.15.Gef.Pb 58.75, CNO 6.14,Py 22.30.

In the determination of fulminic acid, the resulting lead iodide does not interfere. Lead was determined as sulphate but pyridine directly after sublimation with soda in n/10-nitric acid and retitration with n/10-soda lye and bromophenol blue as indicator where neutrality was assumed at pH= 4 as was shown with $PyNO_3$ in water. It results from the large excess of lead -- only one-third is bound to the fulminic acid-- that only 6.14 CNO' + 15.14 Pb+19.75 Py= 41% $Pb(CNO)_2$, 2 Py, with a small excess of the slowly evaporating pyridine, are present.

Consequently, there has probably occurred a lead oxidation with loss of residual fulminate.

The analysis of the ether-moistened product a few minutes after preparation also shows that this is already largely decomposed and only 46 and/or 63% of total lead were bound to the fulminic acid. Its pyridine content calculated for the determined content of CNO produces, per 1 mol $Pb(CNO)_2$ 1.34 to 2.13 mol Py (ref.16) so that here also 2 mol were absorbed which show, however, also partial high tension.

The alkali and alkaline-earth fulminates show, as suspected, no tendency for complex formation to pyridine and are insoluble in the latter.

The ignition temperatures (ref. 17) of all new as well as of the known fulminates were around 150 to 170° for 10 mg substance, i.e. closely above they ignite soon (ref. 18) and in any event within 5 min, the fulminates of alkalies and of the $CH_3 . OH$ - containing barium and strontium-were about 20° lower. Through addition of pyridine, ignition is also lowered by about 20°, except for that of silver which is lower in pyridine and consequently remained unchanged. It may be that, in the others, the oxidizing effect of the fulminic-acid residue on pyridine favors ignition.

NEW SALTS OF FULMINIC ACID - Art. 438

Abstract

1. New double and complex salts were prepared of the composition:

$2Hg(ONC)_2, Na_2S_2O_3$; $Hg(ONC)_2, NaCl$; $Hg(ONC)_2, KBr$; $Zn(ONC)_2, 2NH_3$; $Mn(ONC)_2, 2NH_3$: $Na_2[Ni(ONC)_4]$; $K_5[Co_2(III)\text{-}(ONC)_{11}]$; $Na_2[Pt(ONC)_4]$; $Ca[Pt(ONC)_4]$; $Sr[Pt(ONC)_4]$; $Ba[Pt(ONC)_4]$; $Na_2[Pd(ONC)_4]$; $Na[Au(ONC)_2]$; $Na[Cu(I)(ONC)_2]$.

There were further prepared of the crystal-water containing compounds:

$K_5[Co_2(III)(ONC)_{11}] + 22H_2O$; $Na_2[Ni(ONC)_4] + 5H_2O$;

$Na_2[Pt(ONC)_4] + 5H_2O$; $Ca[Pt(ONC)_4] + 5H_2O$;

$Ba[Pt(ONC)_4] + 3H_2O$; $Na_2[Pd(ONC)_4] + 5H_2O$;

$Sr[Cu(I)(ONC)_2, H_2O]_2$: $Cu(II)[(Cu(I)(ONC)_2, H_2O]_2$;

$Na_2[Cu(I)(ONC)_3] + 3H_2O$; $Ca[Cu(I)(ONC)_3] + 3H_2O$;
$Sr[Cu(I)(ONC)_3] + 6H_2O$; $Ba[CU(I)(ONC)_3] + 4H_2O$.

2. Sodium-aurofulminate was also obtained from alcohol and concentrated nitric acid by the mercury-fulminate process.

3. The authors point out the great similarity of the new fulminates with the corresponding cyanides which suggests the analogous atomic binding of the isocyano-group in the cyanides.

Commercial mercury fulminate always contains more than 1% of impurities. In their investigation, complex fulminates or cyanides were surmised in them. (ref. 2). The constitution of hydrocyanic acid is clarified from a recognition of its extensive analogy with fulminic acid. The expected explosive character of hydrocyanic has already been confirmed for this (ref. 3) and has thus further broadened the analogy between both acids (ref. 4). The preparation of complex fulminates was intended to achieve both objectives. In ref. 1, the pyridine complexes of the fulminates were described among others. Liebig (ref. 5) described cadmium-silver fulminate and the corresponding ammonium magnesium complex was described in ref. 1. Schischkoff (ref. 6) prepared the double salts of mercury fulminate with potassium iodide and (without analysis) with potassium chloride, Steiner (ref. 7) prepared these with potassium cyanide and potassium thiocyanate, and Nef (ref. 8) prepared a sodium-ferrofulminate analogous to the yellow potassium thiocyanide.

As a weak acid, fulminic acid tends like hydrocyanic acid to form complexes. The easy solubility of mercury fulminate in potassium cyanide, in sodium thiosulphate, in potassium iodide, concentrated nitric acid, ammonia, aniline, pyridine, etc. permits this conclusion. Newly defined double salts of mercury fulminate were prepared with $Na_2S_2O_3$, KBr, NaCl, $CaCl_2$, and $MgCl_2$ as well as complexes of zinc and manganese fulminate with NH_3 and also complex salts of sodium and nickel fulminate, potassium and cobalt (III) fulminate, of sodium-platinum (II) fulminate, of the calcium-strontium-and barium-platinum (II) fulminate, of sodium-aurofulminate, of sodium-palladium (II) fulminate; also two types of sodium- and strontium-cuprofulminate as well as calcium- and barium-cuprofulminate and finally the cupric-di-cuprofulminate.

/2749

The preparation of mercury fulminate took place in accordance with Wöhler (ref. 9). The frequently utilized hydrous sodium-fulminate solution is obtained by shaking 7 g mercury fulminate in 30 g water with 20 g of 8-% sodium amalgam (ref. 10) until the solution contains no more mercury ($SnCl_2$ test). Evaporation-drying of the solution is dangerous; even spontaneous temperature rise from splashing with water produced explosion of the dry salt.

The analytical methods were microanalytic (ref. 11) for reasons of safety but also in order to save material and time. Manipulation required certain safety measures -- only $CaCl_2$ or P_2O_5 but never concentrated H_2SO_4 in the dessicator because of the risk of explosion -- because of friction, paper is placed between procelain plate and vessel; pincers and pliers are covered with paper and so are the glass stoppers of the weighing tubes which may also be coated with collodium; do not use glass-stoppered flasks, e.g. for the sodium-fulminate solutions; employ gloves, protective glasses and long-handled flask holders when manipulating large amounts.

a-1) Mercury Fulminate-Sodium Thiosulphate,

$2\ Hg(ONC)_2.\ Na_2S_2O_3$.

10 g mercury fulminate are added to 20 g $Na_2S_2O_3$ dissolved in 40 ccm water and the sediment is filtered. After 24 hours, the solution has solidified into a crystal paste which is drawn off and pressed out on clay. With water, the double salt decomposes into its components. The colorless flakes (dried over $CaCl_2$) darken in a few days and, under heating, they abruptly smolder away without detonation.

$2Hg(ONC)_2$, $Na_2S_2O_3$. Ber. Na 6.33, S_2O_3 15.39, Hg 55.2, ONC 23.08, $Na_2S_2O_3$ 21.72, $Hg(ONC)_2$ 78.28. Gef. (Prod. 1 und 2) Na 6.5, 6.8, $S_2O_3$15.6, 16.4, Hg 53.9, 53.3, ONC (ber. aus Hg) 22.5, 22.3, $Na_2S_2O_3$ 22.2, 23.2 $Hg(ONC)_2$ 76.4, 75.6.

Legend: Ber = theoretical; Gef = experimental; (ber. aus. ..) = calculated from.... Applicable to all specifications given hereafter.

Hydrous $Na_2S_2O_3$ is present in some excess and originates from the mother lye which cannot be elutriated. The Hg-content is too low due to beginning decomposition and the double salt is therefore somewhat impure due to the decomposition product. Mercury was determined microelectrolytically, sodium as Na_2SO_4, and S_2O_3'' as $BaSO_4$ after oxidation with bromium and hydrochloric acid. Titrimetric determination of fulminate is too unreliable since it is not possible to determine how much excess and how much bound thiosulphate in the substance has not yet been changed through secondary reactions.

a-2) Mercury Fulminate-Sodium Chloride, $Hg(ONC)_2$, NaCl

A saturated sodium-chloride solution is saturated at 80° with mercury fulminate and filtered whereupon the flakes (with the sheen of mother-of-pearl) of the double salt precipitate, are filtered and dried on clay but also dissociate through water. Dried above P_2O_5, they are stable and smolder away without detonation upon heating.

$Hg(ONC)_2$, NaCl. Ber. NaCl 17.05, Hg 58.46, ONC 24.49, $Hg(ONC)_2$, 82.95. Gef. (3 Products) NaCl als Cl u. Na best. 19.0, 18.1, 16.9, Hg 54.[illegible], 54.0, 54.4, ONC titrimetr. 22.1-22.6, 22.5, $Hg(ONC)_2$ 74.8, 76.5, 76.0, Hg, nicht an ONC gebunden 2.0, 0.1, 0.7, H_2O 0.9, 1.0. - Sum 96.7, 95.7, 93.6.

The residue of about 6 % of non-difulminate is the decomposition product found by Liebig (ref. 12) after prolonged boiling with alkali chloride of mercury fulminate, i.e. the salt of fulminuric acid, which contains only one-third of the fulminate metal and does not react with thiosulphate. To it must also be ascribed the hygroscopy of the product because neither sodium chloride nor mercury fulminate are hygroscopic in the pure state. Moreover, /275 mercury fulminate does not contain crystal water (ref. 13). It is therefore not very probable that the double salt of either one is hygroscopic in itself.

a-3) Mercury Fulminate-Potassium Bromide, $Hg(ONC)_2$, KBr

From a cold saturated potassium-bromide solution, we obtain, after boiling with mercury fulminate in otherwise analogous preparation, the colorless thin flakes of very similar property. Smoldering here takes place with intense smoke.

$Hg(ONC)_2$, KBr. Ber. KBr 29.49, Hg 49.70, ONC 20.81, $Hg(ONC)_2$ 70.51. Gef. (2 Products) KBr 31.1, 31.1, Hg 48.8, 48.8, ONC titrimetr. 19.2, 19.1, $Hg(ONC)_2$ 65.1, 64.8, Hg (not bound to ONC.) 3.0, 3.1, H_2O 0.8, 1.4, Sum 100.0, 100.4.

Here only 3-% of non-difulminate but an equally large excess of mercury are present and the total sum amounts to about 100. Consequently, this mercury excess is present perhaps as oxide for which less than 0.25 % of oxygen are sufficient. Under intensive conversion to potassium fulminurate according to Liebig, there is actually produced oxide after prolonged boiling.

Double salts of calcium and magnesium chloride prepared in analogous manner are leaf-like crystals of similar properties which were therefore not separately analyzed.

b) Zinc fulminate as well as manganese fulminate so far could not be obtained. Upon evaporation of the aqueous or methyl-alcohol solution (ref. 14), we obtain only a yellow to brown, glassy, highly decomposed and solvent-containing mass. Since NH_3 in the mercury- and the silver-fulminate complex is bound much more loosely than e.g. pyridine -- it does not form any stable compounds like the latter (ref. 14) -- , an unsuccessful attempt was made to arrive at the two salts by way of the solid ammoniates of the two fulminates by removal of the ammonia.

1. Zinc Fulminate-Ammoniate, $Zn(ONC)_2$, 2 NH_3

A solution of 7 g mercury fulminate in 30 ccm of 25-% ammonia is shaken with zinc amalgam (ref. 14) until it no longer contains mercury. The fine colorless prisms which begin to precipitate toward the end of the reaction and increasingly so during cooling, are filtered out, washed with alcohol and ether and dried. The salt deflagrates upon heating with a dull detonation and crackles in the flame. NH_3 is bound so firmly that the salt, even under heating to 200° over phosphorus pentoxide, scarcely loses traces while turning yellow so that pure $Zn(ONC)_2$ could not be obtained from it.

$Zn(ONC)_2$, $2NH_3$. Ber. Zn 35.63. ONC 45.82, NH_3 18.55.
Gef. (2 Products) Zn 35.9, 35.8, ONC 45.7, 45.8, NH_3 18.3, 18.9.

Fulminic acid was determined titrimetric, zinc as zinc-ammonium phosphate, and NH_3 by distillation.

Manganese Fulminate-Ammoniate, Mn(II) $(ONC)_2$, 2 NH_3

The analogous manganese salt must be prepared and precipitated under strict exclusion of oxygen in a nitrogen stream. It must be dried in the vacuum dessicator only when moistened with ether. 3 g mercury fulminate are shaken in anhydrous NH_3-saturated $CH_3 \cdot OH$ with manganese amalgam (Note: Obtained by electrolysis from a solution of $MnSO_4$ on a mercury cathode. Ber. D. Chem. Gesellschaft (62)) This initially forms a brown sediment and, after prolonged shaking, a white incrustation at the wall of the flask. It is immediately filtered through a glass filter into a test tube with lateral projection -- for nitrogen -- which contains some manganese amalgam. Further shaking produces the pure ammoniate as a white powder. After the sediment no longer increases, it is transferred by way of the projection to a second glass filter but on paper as support, drawn off -- without amalgam -- washed with ether and dried in the vacuum dessicator. The yellow salt smells strongly of ammonia (product I) which could, however, be removed only within 1.64 mol after 3 days under vacuum over H_2SO_4 (product II). It then turns dark brown due to decomposition and no longer has any odor. Immediately analyzed, the complex contains 4 mol (3.5 found experimentally) and even this lacks, due to alteration, about 1 % of the amount of manganese calculated from the determination of fulminate. In the test tube, it deflagrates upon heating with a dull detonation. / 2751

$Mn(ONC)_2, 2NH_3$. Ber. Mn 39.5, ONC 60.5, NH_3 19.68. Gef. (2 Prod.) Mn 38.7, 40.8, ONC 61.3, 59.2 NH_3 30.3 (= 3.5 Mol.), 15.6 (= 1.64 Mol.).

Fulminic acid was titrated and manganese weighed as sulphate. The sum of CNO + Mn was equated with 100 in order to be independent of the varying NH_3-content which was referenced to the substance employed.

Attempts to obtain, with the metallic amalgams and/or very finely divided metal powder -- obtained by reduction of the oxides -- from a solution of mercury fulminate in ammoniacal $CH_3 \cdot OH$, the ammoniates of iron, nickel and cobalt fulminate were unsuccessful. Although lead amalgam reacts with the mercury-fulminate solution, the gray deposit which always contains some mercury has only a weak deflagration or simply smolders and is free of ammonia. The ammoniate is evidently very instable and decomposes into non-explosive substances.

c) Complex Salts of the Alkali and Alkaline-Earth Fulminates

The simple cyanides are generally amorphous, not well defined substances and the fulminates are even less stable.

However, the complex cyanides are well crystallized. It was therefore attempted to obtain the complex fulminates and analogies were noted.

1. $Na_2[Ni(II)(ONC)_4] + 5H_2O$ and Anhydrous

Nickel fulminate is not known. Sodium-nickel fulminate is obtained by adding so much nickel-sulphate solution to the sodium-fulminate solution (from 7 g mercury fulminate) that the resulting $Ni(OH)_2$ does not dissolve entirely even under intense shaking. Filtration and vacuum-evaporation over phosphorus pentoxide produces a thick crystal paste. This is drawn off, dissolved in very little water, crystallized in the vacuum dessicator and pressed out between filter paper. The light-brown needles crumble in air, are soluble in water and alcohol but not in ether. Upon heating, the salt decrepitates and, when anhydrous, detonates sharply. The solution of the complex permits recognition and determination, with dimethyl glyoxime, of the nickel ion only after the addition of acetic acid or ammonia. / 2752

$Na_2[Ni(ONC)_4] + 5H_2O$. Ber. Na 12.68, Ni 16.17, ONC 46.30, H_2O 24.85. Gef. (3 Products) Na 12.2, 12.9, 12.8. Ni 16.3. 16.1, 16.1, ONC 46.6, 46.0, 46.4. H_2O 24.9. 25.0 (as difference), 24.7 (exact.).

After fuming evaporation with sulphuric acid, sodium and nickel were weighed together and Ni precipitated with dimethyl glyoxime in ammonia; fulminic acid was titrated according to Philip.

2. $K_5[Co_2(III)(ONC)_{11}] + 22H_2O$ and Anhydrous

A cobalt fulminate is not known. The complex potassium-cobalt (III) fulminate -- the sodium salt is more difficult to obtain pure due to its high solubility - - is obtained in analogous manner from potassium-fulminate solution (Note: Obtained by shaking from 3 g mercury fulminate and potassium amalgam in 5 g H_2O until the solution contains no more mercury) and cobalt (II) sulphate solution until turbidity, followed by filtration and evaporation in the dessicator.

The dark-green starting solution is quickly oxidized by the oxygen of the air to a brown cobalt (III)-solution. The yellow needles are separated from the mother lye by drawing off and recrystallized from very little water. The solution decomposes under heating and gas discharge so that it is necessary to work rapidly. The crystallized salt also turns greenish through decomposition after a few hours. When dehydrated over phosphorus pentoxide, it is stable for a prolonged time. It detonates easily and violently in flame but only crackles when hydrous.

$K_5[Co_2(ONC)_{11}] + 22H_2O$. Ber. K 25.19, Co 15.22, ONC 59.59, H_2O 33.80. Gef. (2 Products) K 26.0, 25.5, Co 15.1, 15.1, ONC (berechn.) 60.2, 59.6, H_2O 33.9, 33.4.

After fuming evaporation of the sulphates, cobalt was determined by electrolysis and fulminic acid calculated from it because the latter cannot be determined directly due to complexity.

A cyanide of analogous formula $(Ag_5Co_2(CN)_{10}NO_2 + 21\ H_2O$, was described by Rosenheim (ref. 15) where the minor difference in water content was conditioned perhaps through the admixture of less hydrous crystals which he actually obtained from concentrated solutions.

3. $Na_2[Pt(II)(ONC)_4] + 5H_2O$ and Anhydrous

So far it has not been possible to obtain either a platinum fulminate nor any complexes of quadrivalent platinum. The sodium-platinum (II) fulminate is produced in well-formed colorless needles if 1 g platinous chloride not containing chloride (Note: Obtained from H_2PtCl_6 by heating to 180-200° for several hours) is gradually added to a sodium-fulminate solution (from 3 g mercury fulminate); the solution is then heated, platinum sponge is filtered from the traces and concentrated in the vacuum dessicator. The needles easily lose their water and the detonate violently in flame whereas they only crackle sharply when hydrous.

$Na_2[Pt(ONC)_4] + 5H_2O$. Ber. Pt 47.70, Na 11.42, H_2O 18.03. Gef. (2 Products) Pt 47.2, 46.9, Na 11.3, 11.6, H_2O 17.6, 18.2.

Na_2SO_4 + Pt were weighed after fuming evaporation with sulphuric acid and the platinum alone after separation of the sulphate. The complex fulminic acid cannot be titrated directly.

Upon dehydration in the dessicator, the colorless / 2753 needles turn dark-red but become colorless again without further change in weight after prolonged exposure to air or heating to 80-100° or moistening with alcohol. The red anhydrous modification is the instable intermediate stage which becomes irreversible during dehydration. The hydrous complex can also originate in two instable types from the solution, as may be seen with evaporation-concentration of a drop. They could not be isolated. There are initially produced at the edge light-yellow needles which are penetrated from the center by long reddish-brown spears which appear blue under incident light and are dichroic. They are quickly converted to the colorless crystals of the stable hydrate described above and are therefore probably instable hydrates of a lower water content because they were in equilibrium with the initially highly over-saturated solution. The hydrates of the complex cyanides of platinum are known to also have such abrupt change of color and dichroism.

4. $Ca[Pt(ONC)_4] + 5H_2O$ and Anhydrous

Calcium-platinum (II) fulminate is produced in not easily soluble, sulphur-yellow prisms when mixing a concentrated solution of sodium-platinum (II) fulminate with calcium chloride. They are also dichroic and blue under incident light. They can be dehydrated over phosphorus pentoxide and then turn dark-green with bronze-green reflections. The hydrous salt emits a yellow-green light under X-rays like the analogous cyanide. It crackles in flame, is hygroscopic and detonates violently when anhydrous.

$Ca[Pt(ONC)_4] + 5H_2O$. Ber. Pt 39.57, Ca 8.12, H_2O 18.25. Gef. Pt 38.4, Ca 8.7, H_2O 17.8.

5. $Sr[Pt(ONC)_4]$. Anhydrous

After mixing of the saturated sodium-platinum (II)-fulminate solution with strontium-chloride solution, the anhydrous and not easily soluble strontium-platinum (II) fulminate crystallizes in dark-red bundles of needles with metallic green sheen. It explodes sharply in flame.

$Sr[Pt(ONC)_4]$. Ber. Pt 43.29, Sr 19.43. Gef. Pt 42.2, Sr 18.2.

The anhydrous salt can also be produced from the warm solution. However, if supersaturation is disturbed by stirring with a glass rod, there are then produced hydrous light-yellow, almost colorless crystals with a slight blue surface sheen which are so instable, however, that they lose their water and turn blood-red even under light pressure between glass slides or filter paper. They emit less light under X-rays than the calcium salt.

6. Ba $[Pt(ONC)_4]$ + $3H_2O$ and Anhydrous

Obtained in similar manner, the not easily soluble barium-platinum (II) fulminate is produced by disturbance of the supersaturation also hydrous in colorless stable prisms which easily lose water in air. The anhydrous salt can be produced directly from a warm solution or when supersaturation is not disturbed, and then occurs in vermilion prisms with blue sheen under reflected light. It emits only little light under X-rays and detonates violently in flame.

$Ba[Pt(ONC)_4] + 3H_2O$. Ber. Pt 38.97, Ba 27.45, H_2O 9.74.
Gef. Pt 38.9, Ba 27.5, H_2O 9.3, 10.3.

Barium and platinum is here calculated for anhydrous substance and water for the starting substance.

7. $Na_2[Pd(ONC)_4] + 5H_2O$

A palladium fulminate is not known. In order to obtain the complex sodium palladium (II) fulminate, 10 ccm of sodium-fulminate solution (from 2 g mercury fulminate) are mixed with 0.5 g $Pd(NO_3)_2$ and filtered. The dark-brown solution is vacuum-concentrated over phosphorus pentoxide. The colorless needles are recrystallized from warm water. They are insoluble in alcohol and easily lose their water in the dessicator. Hydrous salt crackles sharply in flame and the anhydrous salt detonates violently and also on impact.

$Na_2[Pd(ONC)_4] + 5H_2O$. Ber. Pd 25.97, Na 11.20, H_2O 21.93.
Gef. (2 Products) Pd 25.7, 25.8, Na 11.4, 11.3, H_2O 21.4, 21.4.

Sodium was determined as sulphate and palladium after reduction in hydrogen.

8. Na $Au(ONC)_2$

An aurofulminate is not yet known. Sodium-aurofulminate is obtained by preparing sodium fulminate from 1 g mercury fulminate and dilution to 50 ccm, heating to 60° and mixing in drops with gold-chloride solution until permanent turbidity of the dark-brown solution. Upon cooling, the colorless flakes with mother-of-pearl sheen are precipitated (product I). At room temperature, the initially light-yellow solution becomes gradually dark-brown through reduction. The salt is very little soluble in water and explodes upon heating with a sharper detonation than that of the other complex fulminates. It is attacked only very slowly by cold concentrated hydrochloric acid or nitric acid (d = 1.4).

Because of their notable stability to concentrated nitric acid, only mercury and silver fulminate among the fulminates could be prepared so far in the so-called mercury-fulminate process, i.e. from alcohol and concentrated nitric acid. It is now actually possible to obtain sodium-aurofulminate also in this manner. 10 ccm HNO_3 (d = 1.4) are mixed with 15 ccm $C_2H_5 . OH$ (96-%) to which are added 1 g $NaNO_2$ (ref. 16) and 5-10 drops of a concentrated gold-chloride solution. After a few minutes, there occurs a violent reaction as for silver and mercury fulminate and there are produced at the same time the flakes of sodium-aurofulminate (II) already described.

$Na [Au(ONC)_2]$. Ber. Au 64.79, Na 7.56. Gef. (2 Products) Au 64.2, 63.8, Na 7.8, 7.7.

Complex Copper Fulminates

Cuprous fulminate is already known (ref. 17). Of its complexes, there have now been obtained two types, $Me^ICu^I (ONC)_2$ and $Me^I_2Cu^I (ONC)_3$.

9. $Na [Cu(ONC)_2]$

The sodium-copper (I) fulminate of the first type is obtained as anhydrous, colorless, not earily soluble crystal flour by heating 50 ccm of sodium-fulminate solution (from 2.9 g mercury fulminate) to 80°, mixing with 1 g of cuprous chloride, hot-filtering and cooling. It can be recrystallized from warm water. In flame, upon heating in the test tube and upon impact, it detonates violently. /2755.

$Na [Cu(ONC)_2]$. Ber. Cu 37.70, Na 13.67, ONC 48.63. Gef. (2 Products) Cu 37.6, 37.7, Na 13.4, 13.7, ONC 49.0.

Copper was determined by microelectrolysis (ref. 18) and sodium as sulphate; fulminic acid was calculated from a carbon determination effected semi-microanalytically (ref. 10).

10. $Sr[Cu_2(ONC)_4] + 2H_2O$

The strontium-dicuprofulminate of the same type was obtained hydrous in microscopically small colorless crystals by mixing a strontium-fulminate solution (from 1 g mercury fulminate in 10 ccm water by shaking with strontium amalgam (ref. 20)) with 0.5 g of cuprous chloride, heating, filtering and colling. It is not easily soluble in cold but easily soluble in hot water and then decomposes partially by releasing small amounts of $Sr(ONC)_2$ which simultaneously slightly increases the copper values of the recrystallized product, so that product I contains 3.2 % CuONC as excess over the complex whereas product II contains 3.4 % and product III 4.3 %. It is notable that the salt does lose its water either not at all or not very easily in the vacuum dessicator over phosphorus pentoxide, similar to all following complexes of copper (I) fulminate. This may be the reason that it detonates violently upon impact and in flame in spite of the water content.

$Sr[Cu_2(ONC)_4] + 2H_2O$. Ber. Cu 30.35, Sr 20.90, ONC 40.16, H_2O 8.59. Gef. (3 Products) Cu 31.7, 31.0, 30.9, Sr 20.5, 20.0, 19.5, ONC 42.0, ___, ___, H_2O 10.1, ___, ___.

Here also, ONC and H_2O were determined by semi-micro-elementary-analytical combustion with $PbCrO_4$ so that probably less reliable values were found by this.

11. $Cu(II)[Cu(I)_2(ONC)_4] + 2H_2O$

The copper (II)-dicuprofulminate originates from the sodium-copper (I) fulminate solution saturated at 30-40° with excess concentrated $Cu(NO_3)_2$ solution. The light-green lustrous flakes which are not easily soluble, are washed with very little water and alcohol and dried.

$Cu_3(ONC)_4 + 2H_2O$. Ber. Cu 48.31, ONC 42.56, H_2O 9.13. Gef. (2 Products) Cu 48.6, 48.7, ONC 42.0, 42.0, H_2O 9.6, 8.8.

With sodium bicarbonate, only copper (II) is precipitated as green carbonate, whereas copper (I) is determined in the filtrate by electrolysis after addition of nitric acid. The atomic ratio is 1 : 2 in accordance with the formula Cu(II)(Cu(I)ONC + H_2O_2 where, as a consequence of slow spontaneous decomposition by oxidation, the value for Cu(II) becomes slightly too high and that for Cu(I) too low.

Cu(II) [Cu_2(I)(ONC)$_6$] + $2H_2O$. Ber. Cu(II) 16.10, Cu(I) 32.21. Gef. (2 Products) Cu(II) 17.6, 17.9, Cu(I) 31.7, 31.4.

Even upon heating to 80°, the water is not released and therefore has a lesser densitizing influence on the explosive properties of copper fulminate; like the strontium salt, the salt explodes violently whereas the previously described hydrous fulminates only decrepitate. Its initiating action is somewhat less than that of lead azide and mercury fulminate -- probably due to lesser charge density -- but its initial acceleration is very high so that less than 0.02 g are sufficient for the initiation of 0.6 g nitropentaerythrute under a charge pressure of 250 kg/ cm^2 similar to lead azide, whereas 0.15 g are required with mercury fulminate. For the initiation of trotyl, the value lies between that of the two known initiating substances. The occasional explosions-- in the vicinity of mercury-fulminate enterprises -- of buried scrap mercury fulminate (which we know does not to undergo chemical change under these conditions) generally together with scrap detonators in copper cartridges may possibly be ascribed to formation of the copper (I + II) fulminate extremely sensitive to friction which is also formed under exposure to moisture of these detonators in the pit as a green layer and thus presents the risk of explosion in aged stocks of mercury-fulminate detonators. /295

12. [Na_2 Cu(ONC)$_3$] + $3H_2O$

This disodium-cuprous fulminate of the second type of the complex copper fulminates is obtained similar to that of the first type but in concentrated sodium-fulminate solution (from 3 g mercury fulminate in 10 ccm water), without heating and with only about 50 % (0.6 g) cuprous chloride. This dissolves and colorless needles turning bluish under light crystallize upon vacuum-evaporation. It is more easily soluble and does not detonate as easily as the anhydrous fulminate of the first type but explodes in the test tube with a sharp detonation upon heating. Even after several weeks, water is not removed under vacuum over phosphorus pentoxide.

Na_2 [Cu(ONC)$_3$] + $3H_2O$. Ber. Cu 21.95, Na 15.89, ONC 43.50, H_2O 18.68. Gef. (2 Products) Cu 22.2, 22.1, Na 15.9, 15.9, ONC 43.0, 43.1, H_2O 18.4, 18.2.

Sodium was again determined as sulphate, copper by microelectrolysis, and ONC and water by elementary analysis.

13. Ca $[Cu(ONC)_3]$ + $3H_2O$

Analogous to the disodium salt, calcium-cuprous fulminate is obtained from 90 ccm calcium-fulminate solution--corresponding to 3 g mercury fulminate and excess calcium amalgam (Note: By trituration of freshly cut calcium chips with mercury) -- with excess cuprous chloride but by heating to 30-40°, followed by filtering and vacuum-concentration. The solution decomposes so that the large colorless crystals are recrystallized from lukewarm water with the addition of animal charcoal for bleaching. Here also the water is firmly bound so that 0.86 mol (5.5 %) of 3 mol still remained after 8 days under vacuum over phosphorus pentoxide.

Ca $[Cu(ONC)_3]$ + $3H_2O$. Ber. Cu 22.41, Ca 14.13. Gef. Cu 23.1, Ca 14.0.

The salt deflagrates in the flame with red copper vapor and can be detonated by strong impact.

14. Sr $[Cu(ONC)_3]$ + $6H_2O$

Strontium-cuprofulminate is obtained from strontium-fulminate solution prepared from 2 g mercury fulminate by shaking with strontium amalgam in 20 ccm water and by saturating under cold with strontium-dicuprofulminate (described under No. 10) and vacuum-concentration. The large colorless prisms are briefly dried in air. Only 4.5 mol water (21 of 28%) were evaporated under vacuum over phosphorus pentoxide. /225/

Sr $[Cu(ONC)_3]$ + $6H_2O$. Ber. Cu 16.50, Sr 22.73. Gef. (2 Products) Cu 16.8, 17.0, Sr 23.3, 23.4.

Strontium was determined as sulphate like the calcium above.

15. Ba $[Cu(ONC)_3]$ + $4H_2O$

Barium-cuprofulminate is prepared from barium-fulminate solution (from 4 g mercury fulminate in 10 ccm of water by shaking with barium amalgam (Note: By electrolysis from a saturated barium-chloride solution on a mercury cathode at a high current density of 4 A/cm^2)) and excess cuprous chloride which is filtered out before the vacuum-concentration of the solution. The large prisms are recrystallized (eventually with the addition of animal charcoal) from water. Over phosphorus pentoxide, only 15.7 % out of 18 % of the water content had evaporated under vacuum even after 14 days. Its explosive reaction like that of the strontium salt is similar to that described for the calcium compound.

Ba $[Cu(ONC)_3]$ + $4H_2O$. Ber. Cu 15.95, Ba 34.41, ONC 31.59, H_2O 18.05. Gef. (2 Products) Cu 16.0, 16.0, Ba 34.3, 34.4, ONC 31.1, ____, H_2O 18.2, ____.

Like strontium and calcium, barium was determined as sulphate and the fulminate and water by elementary analysis.

Fulminates and Cyanides

If we consider fulminic acid, C : N . OH, and hydrocyanic acid, C : N . H, or a fraction of them (ref. 21) in the same manner as members of the isocyano-group, we then understand their similar odor (ref. 22), their toxicity with similar symptoms, their tendency to polymerization, their explosive capability (ref. 23) and their similar acid strength (ref. 24). Mercuric cyanide must also possess the iso-form of the bond C : N . because it is explosive like other substances (ref. 25) of these atomic bonds -- the isonitriles (ref. 23) -- and is also largely similar to the properties of mercury fulminate. Both are difficult to dissociate in solution, and both attach pyridine, NH_3, NO_3H, CNK, alkali halides, etc. In mercury fulminate, the residual valences are appreciably weaker so that the compounds with NH_3 and NHO_3 cannot be recognized separately but only by the notable solubility. The not easily soluble silver salts of both dissolve in KCN and easily reform the silver salt with acid. In the preceding, we have repeatedly pointed to the similarity of cyanides and fulminates, their low stability, the tendency to formation of complexes and to sodium-ferrofulminate which produces higher-complex salts with such heavy-metal salts as potassium ferrocyanide. The similarity in the alkali and alkaline-earth complexes of both acids is further shown for nickel (II), cobalt (III), platinum (II), palladium (II), gold (I), and copper (I). Particularly striking here is the similarity / 27 of the complexes of gold and platinum in regard to solubility, dichroism, brilliant color and color variation under isomerism and variation of hydration, the notable metallic lustre and bronze sheen of many complexes and the luminosity under X-radiation. Precisely the latter points to the structural similarity of the salts of both acids.

Literature References

1) 1. Mitteil.: B. 38, 1356 1905 ; 2. Mitteil.: B. 50, 586 1917 .
2) L. Wohler, B. 38, 1356 1905 .
3) Ztsch. ges. Schieß- u. Sprengstoffwesen 7, 181 1912 ; C. 1912, II 874.
4) Heaven, Journ. Soc. chem. Ind. 37, 143 1918 ; C. 1919, II 703.

5) Weber, Dissertation (manuscript), Darmstadt 1920.
6) Gutmann, B. 39, 509 1906 .
7) cf. Dissertat. Weber, Darmstadt 1920 (Manuscript).
8) Dunstan, Bossi, Journ. chem. Soc. London 73, 360 1898 .
9) Wieland, B. 42, 1347 1909 .
10) B. 12, 2162 1879 ; Nef. A. 287, 347 1895 .
11) Steiner, B. 7, 1244 1874 , 8, 518 1875 .
12) Gazz. chim. Ital. 27, 50 1897 .
13) Compt. rend. Acad. Sciences 136, 947 1903 .
14) Varet, Bull. Soc. chim. France 3 5, 949 1891 ; Weith, Ztschr. Chem. 1869, 380.
15) L. Wohler und Martin, B. 50, 589 1917 .
16) Details, cf Berthmann, Dissertat., Darmstadt 1927.
17) Figures, cf. Dissertat. Weber, Darmstadt 1920.
18) L. Wohler und Martin, Ztschr. angew. Chem. 30, 34 1917 .

1) Mitteilung 62, 2472 1929 .
2) To be published later elsewhere.
3) L. Wohler und Roth, Chem. Ztg. 50, 761, 781 1926 .
4) Nef, A. 280, 312, 334 1894 .
5) Ann. Chim. 24, 315 1823 .
6) A. 97, 55 1856 .
7) B. 9, 786 1876 .
8) A. 280, 334 1894 .
9) Kast, Explosive and Detonating Substances (1921), p. 412.
10) A. 280, 307 1894 .
11) s. Dissertat. Berthmann, Darmstadt 1927.
12) A. 95, 283 1855 ; s. a. A. 97, 55 1856 .

13) Berthmann, Dipl.-Arb. Darmstadt, Mai 1926, S. 15. Kast und Selle, B. 59. 1958 August 1926 .

14) Wohler und Martin, B. 50, 591 1917 ; s. auch die 3. Mitteil.

15) Ztschr. anorgan. Chem. 17, 68 1898 .

16) L. Wohler, B. 38, 1358 1903 .

17) L. Wohler, B. 50, 591 1917 .

18) Pregl, Quantitat. organ. Mikro-analyse 1917 , S. 142.

19) Approximately in the variant described by Berl, Schmidt, and Winnacker, Chem. Ber. 1928 (61) 83.

20) Obtained by electrolysis on mercury cathode from strontium-chloride solution.

21) On tautomerism also of fulminic acid, cf. Palazzo, C(Chemie?) 1913 (I) 1101.

22) Nef, A. 280, 305, 312 1894 ; Schischkoff, Ann. Suppl. 1, 109 1832 .

23) L. Wohler und Roth, l. c.

24) L. Wohler, B. 38, 1356 1905 .

25) L. Wohler, Ztschr. angew. Chem. 35, 548 1922 .

TRANSLATED BY
TRANSLATION & INTERPRETATION
DIVISION
*
THE INSTITUTE OF MODERN LANGUAGES, Inc.
Washington, D.C.