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TETRANITROMETHANE AND RELATED COMPOUNDS

by

Thomas J. Tully

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## TETRANITROMETHANE AND RELATED COMPOUNDS

Tetranitromethane was first prepared by Schischkow in 1861 (1), but has been put to little practical use since that time. This is due in part to the reluctance that many chemists have for working with highly nitrated compounds and the general feeling that tetranitromethane, due to its very high nitrogen and oxygen content, should be relatively unstable and dangerously explosive. These fears are unfounded, since pure tetranitromethane is a very stable compound which is not detonated by heat or impact.

During the latter part of World War II, some interest in tetranitromethane developed in Germany. Experiments were run on the use of tetranitromethane as an oxidizing agent in rocket engines and as an additive in Diesel fuels to increase the cetane number.

Since the last war, interest has developed in new types of engines and devices for propelling objects in mediums other than the ordinary atmosphere, such as under water or above the stratosphere. This has intensified the search for combustion-supporting materials of high potency. These new developments, as well as the search for new and more powerful high explosives, have caused some demand for such compounds as tetranitromethane, nitroform, and trinitroacetonitrile.

The present investigation was initiated in 1947 and is being continued at the present date. The object was to establish a source of supply of tetranitromethane for workers engaged on research and development projects for the government and to develop safe methods for the preparation, purification, handling, storing, and shipping of tetranitromethane and related compounds. Most of this work has been accomplished successfully and, as a result of the present investigation, tetranitromethane of high purity is now being made in semi-commercial quantities.

### Historical

While engaged in the study of mercuric fulminate in 1857, Schischkow (2) heated that compound with a solution of sodium chloride and obtained sodium fulminate. This substance was used as the starting point for the preparation of trinitroacetone nitrile, nitroform, and tetranitromethane by the following procedures:

Sodium fulminate was added in small portions to a mixture of equal volumes of fuming nitric acid and concentrated sulfuric acid. As the liquid became warm, carbon dioxide was evolved and an oily layer of trinitroacetone nitrile formed on the surface of the acid:



The oily layer was solidified by cooling, placed in a retort and distilled in a current of dry air at about 60°C. Pure trinitroacetone nitrile was collected in the neck of the retort

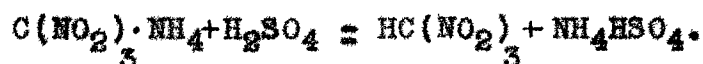
as a white, volatile solid that melted at 41.5°C. and exploded when quickly heated to about 220°C.

The trinitroacetone nitrile was rapidly hydrolyzed by hot water forming carbon dioxide and the ammonium salt of nitroform:



The salt was obtained as well defined yellow crystals by evaporating the yellow solution.

Schischkow obtained nitroform by treating the ammonium and potassium salts with sulfuric acid:



The nitroform was obtained as colorless crystals which were solid below 15°C. Although the substance had a rather high vapor pressure, it could not be distilled since it decomposed rather violently at about 100°C.

In 1861 Schischkow treated nitroform with a mixture of nitric and sulfuric acids at 100°C. A stream of air was led through the mixture and a liquid distilled over. When the distillate was diluted with water, tetranitromethane separated as a heavy liquid. This was washed with water and distilled, yielding a product boiling at 126°C., and solidifying to a crystalline mass at 13°C.



Pictet and Grenequand (3) in 1903 obtained small amounts of tetranitromethane by the interaction of acetic anhydride and diacetylorthonitric acid. They also found that traces of tetranitromethane were produced when fuming nitric was added to acetic anhydride, but the reaction was dangerously violent, frequently resulting in explosions accompanied by flame.

Hantsch prepared tetranitromethane by the interaction of iodopierin and silver nitrite in 1906. (4).

In 1907 Pictet and Khotinsky (5) obtained tetranitromethane from acetic anhydride and acetyl nitrite and, during the same year, Classen (6,7) patented a process for obtaining the same compound by heating aromatic hydrocarbons and their derivatives such as nitrobenzene with a large excess of a mixture of nitric and sulfuric acids containing sulfur trioxide.

Schenck prepared tetranitromethane in satisfactory yield by slowly dropping acetic anhydride into a mixture of nitrogen pentoxide and nitrogen peroxide. He protected his process by two patents in 1908. (8).

The first practical method for the preparation of tetranitromethane was developed by Chattaway in 1910. The method consisted of the slow addition of acetic anhydride to fuming nitric acid, d. 1.53, at a temperature of 20° to 25°C. The mixture was allowed to stand for a week and was then diluted with water. The bulk of the tetranitromethane was obtained as a heavy oily layer at

the bottom. An additional amount was obtained by the steam distillation of the dilute acetic acid from the upper layer. The product was purified by washing with water and dilute sodium carbonate and was finally dried over fused calcium chloride. An 80% yield was claimed.

Chattaway first disclosed his process in a paper read before the Chemical Society in England on June 16, 1910 (10) and published a paper later that year. He also wrote a survey of the work done on tetranitromethane and nitroform prior to 1910. (11).

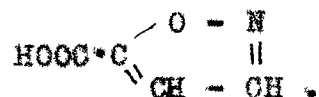
Within a few weeks of the presentation of Chattaway's paper, the Farbenfabriken vorm. F. Bayer u.Co. disclosed a similar method for the preparation of tetranitromethane and obtained patents in both Germany and Britain. (12).

Further work on the preparation and constitution of tetranitromethane was done by Will in 1914. (13)

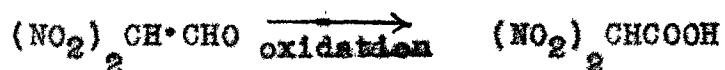
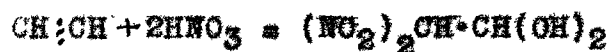
A new method for the preparation of both nitroform and tetranitromethane based on the nitration of acetylene was discovered by Orton and McKie (14) in 1920. The reaction of acetylene with fuming nitric had been studied by Baschieri (15), Testoni and Mascarelli (16), and Schmidt (17) between 1900 and 1904. Although Schmidt obtained a small amount of nitroform, the chief product of these researchers was a solid explosive compound having the composition  $C_4H_3O_3N$  and a melting point of  $149^{\circ}C$ . This



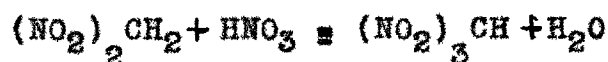
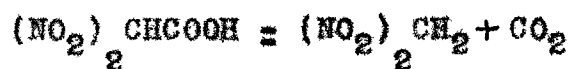
compound was studied by Quilico and Fereri (18) in 1930 and identified as an isoxazole- $\alpha$ -carboxylic acid of the formula,



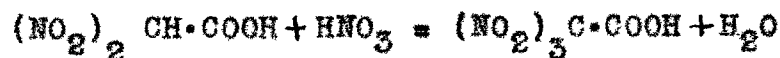
The method of Orton and McKie consisted in bubbling acetylene gas through fuming nitric acid containing a small amount of mercuric nitrate. The gas was readily absorbed and converted to nitroform which remained dissolved in the nitric acid. This could be extracted with ether or further nitrated to tetranitromethane by heating the nitric acid solution with concentrated sulfuric acid. The following equations were proposed to explain the reactions:



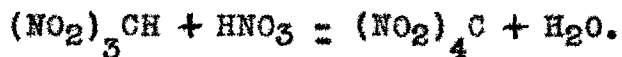
then either:



or:



Then, when heated with sulfuric acid, the nitroform was nitrated to tetranitromethane:



Based on these equations, a yield of 59.2% was obtained, calculated on the amount of acetylene used. The freezing points of the samples of tetranitromethane obtained in these experiments were from 13.0° to 13.5°C. This seems to be the first time that a freezing point above 13.0° was reported.

A similar method for preparing tetranitromethane by bubbling ethylene through 95% nitric acid containing mercuric nitrate, followed by heating with sulfuric acid was reported by McKie in 1927 (19a). The yield was lower than that obtained with acetylene.

The compound was also prepared by the action of nitric acid on dinitrobenzene by McKie in 1925 (19b).

Tetranitromethane is formed as an undesirable by-product in the nitration of toluene to trinitrotoluene. Methods for separating it from the TNT by vaporization have been patented by Classen (6) in 1905 and Gartner in 1927 (20).

Prior to 1935, the work done on tetranitromethane was on a small laboratory scale. During that year Hurd, working at the Trojan Powder Company, added such compounds as phosphoric acid, phosphorus pentoxide, phosphorus oxychloride, phosphorus trichloride, phosphorus pentachloride,

sulfuric acid, sulfuryl chloride, boron triacetate, acetyl chloride, hydrochloric acid, or mixtures of these to mixtures of nitric acid and acetic anhydride. The process was a modification of that described by Chattaway in 1910. (9,10,11). He also used sharp angular pieces of quartz, glass, or like materials in the reaction mixture. Hurd claimed that these additions increased the yield of tetranitromethane to 85%, decreased the amount of by-products, and led to a smoother reaction. A patent application was made on January 29, 1936 and a patent was granted on October 13, 1936. (21). Several hundred pounds of tetranitromethane were produced at the Trojan Powder Company. The material was unstable and turned dark in storage. The chief impurity in the material that had been in storage for fifteen years was found to be nitrogen tetroxide which could be removed quite readily by washing with dilute sodium carbonate and water. The washed product still contained some impurities, since the freezing point range was 13.2° to 12.1°C. The material was not sensitive to impact either before or after the washing (22).

During World War II, an interest in tetranitromethane developed from the idea that it could be used as a substitute for nitric acid in rockets. It was thought that the use of tetranitromethane would overcome the corrosion problem that attended the use of nitric acid.

It had also been found that the addition of 0.5 to 1.0% of tetranitromethane to Diesel fuel increased the cetane number by 10 to 15 points.

About 1943 the German government commissioned the I.G. Farbenindustrie at Frankfurt-Hoechst to manufacture a large quantity of tetranitromethane without regard to yield or cost, and to develop an economical process to supply the material for future use. The work was done by Schultheiss, Schimmelschmidt, and Reuter and has been summarized in British and American government reports by Hunter (23), Hurd (24), and Richardson (25), and more recently by Hager (26).

Using the method of Chattaway (9,10,11), ten tons of tetranitromethane were produced in a short time but the workers claimed that the product was impure and unsafe to handle. They stated that they were unable to produce a product of high purity by the nitration of acetic anhydride. No effort was made to recover the acetic acid formed in the process. Due to the high cost and the low quality of the product, the process was finally abandoned.

The German workers next developed a continuous process for making tetranitromethane from acetylene. They used the method of Orton and McKie (14) and modified it in several ways. The raw materials were fed continuously and the tetranitromethane was finally washed with sulfuric acid in a counterflow tower.

The entire equipment was made of glass and designed to produce ten kilograms of tetranitromethane per day. The product was of greater purity than any of those described in the literature prior to that time. The material produced in the regular runs had a melting point of 13.8° to 14.0° C. The workers prepared some tetranitromethane that had a melting point of 14.2° C. and reported that figure as the melting point of the pure compound. The work was discontinued at the end of the war.

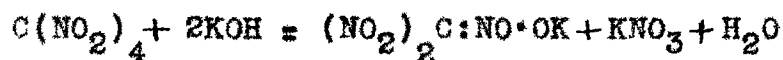
Pure tetranitromethane is a colorless liquid with a high index of refraction. It has a density of 1.65 grams per ml. at 15° C. It solidifies at 14.2° C. and boils at 126° C. It has a high vapor pressure for a compound of such high molecular weight. Mensies (27) gave the following pressures for the temperatures indicated:

<u>t° C.</u>	<u>pres. m.m.</u>
50	44.2
55	56.1
60	70.6
65	88.1
70	109.0
75	134.0
126	760.6

The vapors of tetranitromethane are very irritating and cause much discomfort when breathed in small quantities. There is little doubt that they are quite poisonous.

Tetranitromethane is stable when pure and is not detonated by heat, impact, or the explosion of a number six detonator cap. However, its mixtures with aromatic hydrocarbons are very powerful explosives which are usually more sensitive to shock than nitroglycerine. Tetranitromethane forms explosive compounds or mixtures with a wide variety of combustible materials. It can be dissolved with safety in carbon tetrachloride, but it should not be mixed with organic substances that are readily oxidized. When initiated by a number six cap, paper and sawdust wet with tetranitromethane detonate with great violence and are about as sensitive to shock as tetryl.

The structure of tetranitromethane has been the subject of a controversy. It reacts with potassium hydroxide in two ways, the type of reaction depending on the concentration of the base. With concentrated potassium hydroxide, the potassium salt of nitroform and potassium nitrate are obtained in almost quantitative yield, while dilute solutions of potassium hydroxide transform a considerable amount of the tetranitromethane to potassium carbonate and potassium nitrite:



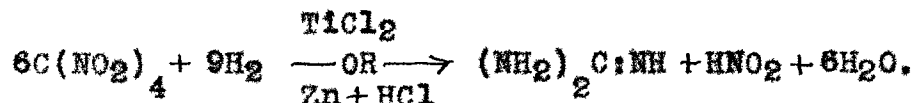
There is also some indication that tetranitromethane is hydrolyzed in acid solution to form nitrous acid since, under these conditions, it reacts with dimethyl aniline to form the para nitroso derivative.

The fact that one nitro group in tetranitromethane seems to react preferentially led Schmidt (28) to conclude that the compound does not contain four nitrogroups but is the nitrous ester of trinitromethyl alcohol;



or a mixture of this with the tetranitro compound. This theory has been supported by Robinson (29). However, Weissberger and Sangewald (30) have shown that the dipole moment of tetranitromethane in carbon tetrachloride solution is zero. This and the investigations of Lewis and Smith (31) as well as those of Mark and Noethling (32) prove that tetranitromethane has a symmetrical configuration and is a true tetranitro compound.

Tetranitromethane is reduced to guanidine by zinc and hydrochloric acid (33) and by titanous chloride (34):



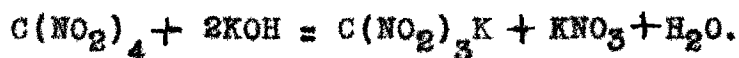
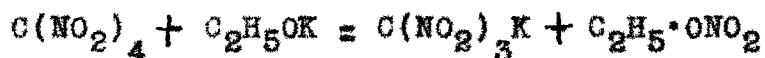
Phenyl hydrazine yields a salt of mononitromethane (35):



Tetranitromethane forms bright colored compounds with unsaturated compounds. This reaction has been used for the detection of ethylene bonds (36 to 49).

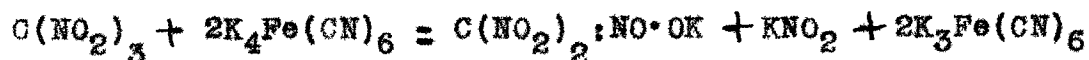
### Nitroform

Although nitroform was originally prepared by the hydrolysis of trinitroacetonitrile and is readily nitrated to tetranitromethane, it is most conveniently prepared by the alkaline reduction of tetranitromethane. One nitro group is readily replaced by a metal to yield a salt of nitroform. This reduction was discovered in 1899 by Hantsch and Rinckenberger who used potassium ethoxide and potassium hydroxide as reducing agents (50):



Concentrated aqueous sodium hydroxide was used by Schmidt (29). The reactions of tetranitromethane with strong alkalies or alkali metal alcoholates may be violent and sometimes result in explosions (51).

Chattaway and Harrison (52) in 1916 used potassium ferrocyanide as a reducing agent and obtained the relatively insoluble potassium salt of nitroform by a smooth reaction which offered no difficulty.



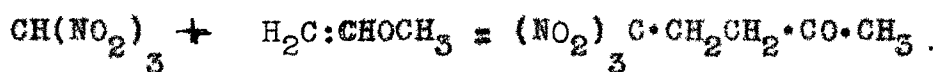
Other reducing agents that have been used are liquid ammonia, hydrazine, sodium phosphate and sodium potassium tartrate (53,54,55,56,57). Nitroform can also be prepared with safety by shaking tetranitromethane with aqueous potassium hydroxide and glycerol (58).



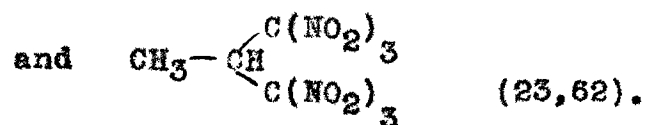
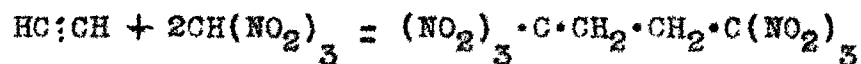
Nitroform is a colorless liquid that freezes to a white solid at 23°C. When heated, it decomposes violently at about 100°C. and may explode when heated suddenly to higher temperatures. It boils at 45° to 47°C. under a pressure of 22 m.m. The compound has a strong, irritating odor and attacks the eyes and nose.

Nitroform is soluble in water, alcohol, ether, carbon tetrachloride, and most organic solvents. In non-ionizing solvents its solutions are colorless and the compound exists as a true nitro compound;  $\text{HC}(\text{NO}_2)_3$ . Its water solution is bright yellow in color and is strongly acidic, the compound existing in the ionized aci-form;  $\text{H}^+ \text{ } ^-\text{O}\cdot\text{NO};\text{C}(\text{NO}_2)_2$  (59). The mercuric salt of nitroform is a colorless solid easily soluble in ether, benzene, and chloroform, giving colorless solutions. It is deliquescent in ether vapor. (60). The solutions of mercuric nitroform in alcohols and aliphatic ketones are pale yellow, and solutions in water and pyridine are deep yellow (61).

Nitroform reacts with unsaturated compounds to form trinitromethyl-substituted compounds, many of which are explosive. It adds, for instance, to methyl vinyl ketone to form gamma-trinitropropyl methyl ketone, an explosive compound comparable in power to R.D.X.



It unites with acetylene in the presence of mercuric nitrate to form a mixture of hexanitrobutanes. These are very powerful and dangerous explosives.



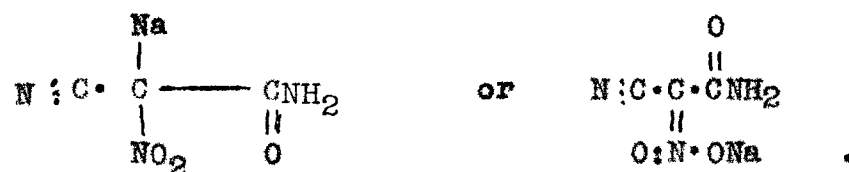
### Trinitroacetoneitrile

Schischkow (2) first prepared trinitroacetoneitrile in 1857 by the action of fuming nitric and sulfuric acids on sodium fulminate.

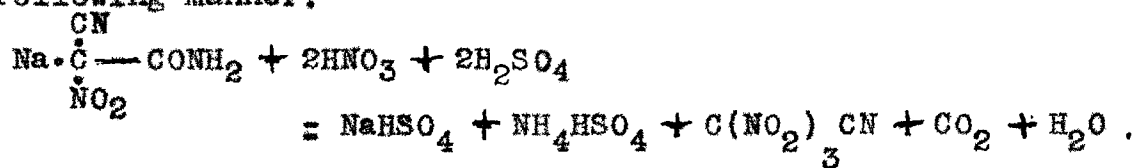
Fulminuric acid is the mononitro derivative of cyanoacetamide,



It is a monobasic acid and forms salts in which the metal may be attached to the central carbon atom or to one of the oxygen atoms of the nitro group:



The sodium salt reacts with nitric and sulfuric acids in the following manner:



Trinitroacetonitrile forms soft colorless crystals which are very volatile. It resembles camphor in appearance, melts at 41.5°C., and explodes when heated quickly to 220°C. The vapor has a strong disagreeable odor and is very irritating to the eyes, nose, and throat.

Trinitroacetonitrile reacts with water to form ammonium nitroform which forms a bright yellow solution:



Schischkow (1) prepared the ammonium salt of nitroform by heating trinitroacetonitrile with water. Although the reaction usually proceeded smoothly, Mayer (63) reported that, in one experiment which was performed under the same conditions as several others, a violent explosion occurred. The reason for this explosion could not be explained.

Although no other method for the preparation of trinitroacetonitrile has been reported, it might be assumed that it could be prepared from cyanoacetamide. Migrdichian (64) states that isonitrosoacyanoacetamide can be formed by treating cyanoacetamide with sodium nitrite and acetic acid; and Conrad and Schulze (65) report that they oxidized isonitrosoacyanoacetamide to fulmunuric acid by treatment with potassium permanganate:



## Present Investigation

The chief purpose of the present investigation was to develop a safe method by which a pure grade of tetranitromethane could be prepared and to establish a source of supply of the material in the shortest possible time. The cost of the material and the yield were of secondary interest.

After a few initial experiments with the acetic anhydride method of Chattaway (10) and the acetylene method of Orton and McKie (14), it was decided that the former method would be more suitable. In the first experiments, the method given in Organic Synthesis (66) was used but the size of the batch was doubled. Experiments were run using the following acids:

Red fuming nitric acid (99.98%)

Yellow fuming nitric acid (90.06%)

Anhydrous nitric acid (99.99%) prepared by distilling the yellow fuming acid from an equal volume of 95.6% sulfuric acid and collecting the fraction boiling at 85° to 86.5°C.

Although the anhydrous nitric acid gave higher yields, the red fuming acid was selected for the work, since it could be obtained readily from several chemical supply houses. The various acids gave the following yields of tetranitromethane:

<u>Acid</u>	<u>Yield % theory</u>
Yellow fuming	34.8%
50% red fuming 50% yellow fuming	43.8%
Anhydrous	57.3%
Red fuming	49.8%

The yield was about the same with commercial acetic anhydride as with the chemically pure grade.

It was soon found that lower yields were obtained in larger batches. If the temperature of the batch rose above 30°C., NO<sub>2</sub> fumes were evolved and most of the product was lost. This reaction can be quite violent and the temperature may rise rapidly. When batches were iced for several days and then allowed to warm up to room temperature, the reaction became violent and most of the product was lost.

The reaction runs most smoothly and gives the best results when the acetic anhydride is run into red fuming nitric acid with mechanical stirring, the temperature being held at 20 to 25°C. The rate of addition depends on the efficiency of the cooling. The temperature tends to rise rapidly when the addition is first started and the rate of addition must be slow. After about 25% of the acetic anhydride has been added, the reaction is less violent and the rate of addition can be increased. The addition usually requires about an hour, but can be shortened to as low as twenty minutes by efficient cooling.

After the addition, the temperature of the batch should be held between 20 and 25°C. for a week. This can be done best on a laboratory scale by keeping the batch in running water for one day and then in a rather large volume of still water for the remainder of the week. The level of the cooling water should be above the level of the batch in the vessel, otherwise heat developed in the upper part of the liquid will cause the batch to fume.

This reaction may generate enough heat to become quite violent. On one such occasion, a three-gallon glass bottle, in which a large laboratory batch had been prepared, cracked completely around at the surface of the cooling water. This could be quite dangerous, since water, mixing with batch during the first 24 hours, causes a very violent reaction. Fumes of  $\text{NO}_2$  are evolved and the acid may spatter. Consistently good results can be obtained when the temperature is regulated properly.

In the early part of the investigation, the tetranitromethane was separated and purified by the method given in Organic Synthesis (66). The nitration mixture was diluted with water and steam distilled. The distillate separated into two layers, with the tetranitromethane on the bottom. The volume of the bottom layer was usually about 25% of the total distillate. After separating, the tetranitromethane was washed with 0.25 normal sodium carbonate and then two or three times with water, and finally dried with anhydrous sodium sulfate. The product had a freezing point of  $13.5^\circ\text{C}$ .

During the investigation a new and very useful method of purification was developed. After the steam distillation, the product was given one wash with water, one with 0.25 normal sodium carbonate, 2 washes with water, and then shaken with concentrated sulfuric acid. This method gave an excellent product which was very light in color and froze at  $14.2$  to  $14.0^\circ\text{C}$ . Almost all of the sample solidified at  $14.2^\circ\text{C}$ . and there was only a small amount of liquid left when the temperature

went lower. This method has given consistent results with laboratory and pilot plant batches.

After being treated with sulfuric acid, the tetranitromethane frequently has a slightly opalescent appearance. This is due to a very small amount of sulfuric acid that remains in dispersion. It was found that the acid can be removed readily by shaking the liquid with anhydrous sodium sulfate.

The tetranitromethane prepared by this process is purer than that produced by other practical methods.

#### Sensitivity of Tetranitromethane to Heat and Shock

A sample of tetranitromethane, having a freezing point range of  $14.2^{\circ}$  to  $14.0^{\circ}\text{C}$ ., was tested for sensitivity to heat by placing single drops of the substance on a heated steel plate at  $300^{\circ}\text{C}$ . and at red heat. Although the substance decomposed and evolved  $\text{NO}_2$  in each test, it did not explode or ignite, even at red heat.

When samples of paper, wood, sawdust, and absorbent cotton were wet with tetranitromethane and ignited, they burned very rapidly but did not explode. A sample of tetranitromethane in a glass bottle, closed by a screw cap, was placed in a wood fire. When the bottle burst, the fire flared brightly for a few seconds. There was a swishing sound but no explosion.

The sensitivity of tetranitromethane to shock was tested on a drop test apparatus using an eight pound weight.

Pure tetranitromethane could not be exploded by a 24 inch drop of the weight, which was the maximum capacity of the instrument. Sawdust wet with tetranitromethane proved about as sensitive to impact as tetryl and R.D.X. and somewhat less sensitive than nitroglycerine.

Samples of sawdust and paper toweling wet with tetranitromethane gave high order detonations when initiated by number six electric blasting caps. In each case the explosion was accompanied by a bright yellow flash and very little smoke. In a like test, absorbent cotton gave a low order explosion and a considerable amount of  $\text{NO}_2$ . After the explosion, about half of the cotton, still wet with tetranitromethane, was found unchanged. Pure tetranitromethane was not exploded by a number six electric blasting cap fired in the liquid.

These tests proved that, although the tetranitromethane is not explosive, it is very dangerous when mixed with combustible materials.

Tests have proved that pure tetranitromethane has no effect on sheet aluminum, bakelite, or polyethylene. The compound is now being shipped in aluminum bottles sealed with bakelite screw caps and polyethylene disks.



### Nitroform

Two methods for the reduction of tetranitromethane to potassium nitroform were used during the investigation. The first was that of Chattaway and Harrison (52), using potassium ferrocyanide, and the other was a modified method similar to that of Muraour (55), using sodium sulfite and potassium hydroxide. Good yields were obtained in both experiments.

A new method for preparing nitroform in carbon tetrachloride solution was developed. A suspension of dry potassium nitroform in carbon tetrachloride was treated with dry hydrogen chloride. Potassium chloride was formed and a solution of nitroform in carbon tetrachloride was obtained.

### Trinitroacetonitrile

Since trinitroacetonitrile is readily converted by hydrolysis to the ammonium salt of nitroform, several attempts were made to prepare it by new methods. Although most of the experiments were unsuccessful, two new methods for the preparation of trinitroacetonitrile were developed. Attempts to nitrate acetonitrile to the trinitro compound with red fuming nitric acid or yellow fuming nitric acid both with and without concentrated sulfuric acid were unsuccessful. The addition of mercuric nitrate did not help. When acetonitrile was treated with a mixture of red fuming nitric acid and acetic anhydride, the nitric acid seemed to

to have reacted with acetic anhydride rather than with the acetonitrile, and tetranitromethane was formed.

The treatment of cyanoacetamide with a mixture of red fuming nitric acid and concentrated sulfuric acid led to the formation of trinitroacetoneitrile. In the first experiment the temperature rose suddenly, the batch fumed, and most of the product was lost. Another experiment was run with better control. The temperature was held below 18°C. and a 72.4% yield of trinitroacetoneitrile was obtained. The product after being purified by sublimation had a sharp melting point at 41.4°C. corrected. The literature gives the melting point as 41.5°C. The formation may be represented by the following equation:



When treated with water, the compound turned bright yellow on the surface and a bright yellow color dissolved in the water. This color was due to the formation of the ammonium salt of nitroform:



The reaction with water at room temperature was not very rapid. The hydrolysis of 5 grams of trinitroacetoneitrile in 100 ml. of water at room temperature required about 36 to 48 hours. The completion of hydrolysis is indicated by the disappearance of both the solid phase and odor of trinitroacetoneitrile. Heating to 80°C. did not help, since much of the volatile trinitroacetoneitrile was lost.

V. Meyer reported that a violent explosion occurred in one experiment when trinitroacetonitrile was heated with water (42). The reason for the explosion could not be explained. Both Meyer and Schischkow (2) prepared ammonium nitroform in this manner.

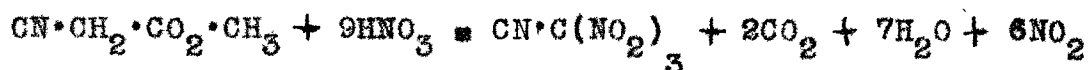
In the present investigation, several samples of trinitroacetonitrile have been heated in water to 80°C. with no indication of violent reaction or explosion. However, better results were obtained when the compound was left in contact with water at room temperature for several days.

The water solution of ammonium nitroform is stable and can be kept in a stoppered flask for months.

A second new method for the preparation of trinitroacetonitrile was developed during the investigation. Cyanoacetic acid was added to a stirred mixture of red fuming nitric acid and concentrated sulfuric acid. The temperature was held below 23°C. Carbon dioxide was evolved and solid crystals of trinitroacetonitrile separated:



Attempts were made to prepare trinitroacetonitrile from methylecyanoacetate and acrylonitrile according to the following equations:



Both methylecyanoacetate and acrylonitrile reacted with a mixture of red fuming nitric acid and concentrated sulfuric acid. A gas was evolved in each case, but no trinitroacetonitrile could be separated from the products of either experiment.

#### Freezing Point Depression Experiments on Tetranitromethane

Due to its high freezing point ( $14.2^{\circ}\text{C}.$ ), tetranitromethane is not suited for use in high altitude rockets. During World War II, the Germans found that a mixture of 30% nitrogen peroxide and 70% tetranitromethane had a freezing point of  $-27^{\circ}\text{C}.$  (23,62). Ten tons of the mixture were prepared and sent to Peenemunde for testing. Some corrosion problems were encountered, but further information on the tests does not seem to be available.

The molal freezing point lowering was reported verbally (22) as about  $35^{\circ}\text{C}.$  per mole of solute in 1000 grams of tetranitromethane. The origin of this statement could not be determined nor could the figure be verified experimentally.

It was thought that solutions of strong oxidizing agents, such as nitrogen peroxide or chlorine, in tetranitromethane, might have low freezing points and high oxidizing potentials, and might be suitable combustion supporting agents for rocket propulsion.

The solubility of chlorine in tetranitromethane at one atmosphere and room temperature was too low to make it useful.

A solution of 28.8% nitrogen peroxide in tetranitromethane started to freeze at  $-21.5^{\circ}\text{C}$ . This was not very stable and lost nitrogen peroxide readily.

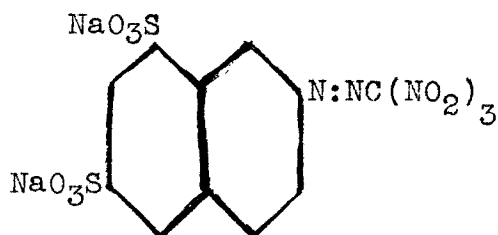
A solution consisting of 10% glacial acetic acid and 90% tetranitromethane was found to have an initial freezing point of  $5.7^{\circ}\text{C}$ . Since glacial acetic acid is not a pure compound and contains some associated molecules, the results of this experiment could not be used to determine the molal freezing point depression rate for tetranitromethane. The mixture did not explode under the impact of a 500 gram weight falling 100 centimeters. Stronger solutions of acetic acid were not used since it was feared that they might be explosive.

The molal freezing point depression rate for tetranitromethane was determined using carbon tetrachloride as a solute. The rate was found to be  $10.0^{\circ}\text{C}$ . per mole of solute in 1000 grams of tetranitromethane.

Attempt to Prepare an Azo Compound  
of Nitroform

A suspension of potassium nitroform in water was treated with a suspension of diazotized amino G salt in the presence of sodium acetate. It was thought that an azo

compound of the following structure might be formed:



This might prove to be a water soluble dye.

A bright yellow solid, soluble in water, was obtained but, on standing overnight in liquid of the batch, it decomposed, forming a dark brown solution.

The instability of the compound confirms the work done by Ponzio (67) who treated ammonium nitroform with aromatic diazo compounds and obtained crystalline products which were yellow to orange in color. He claimed that these were azo compounds of the type  $\text{pCl}\cdot\text{C}_6\text{H}_4\cdot\text{N}=\text{N}\cdot\text{C}(\text{NO}_2)_3$ . The products were very unstable and decomposed rapidly on standing, either by themselves or in solution.

In this new attempt to prepare an azo derivative, it was thought that the presence of the sulfonic groups in amino G salt might have some stabilizing effect on the product, but this idea was not verified by the results of the experiment.

Experimental:

Preparation and Purification  
of Tetranitromethane

Commercial acetic anhydride (97 to 100%) weighing 204 grams was added slowly to 126 grams of red fuming nitric acid ( $d = 1.59$ ) in an Erlenmeyer flask. The flask was set in a copper water bath which was packed with finely chopped ice. The acid was mechanically agitated during the addition. The first 25% of the acetic anhydride was run in dropwise, since a considerable amount of heat is generated in the early stages of the addition. The remainder was added more rapidly. The temperature was held between  $17^{\circ}$  and  $21^{\circ}\text{C}$ . by regulating the rate at which the acetic anhydride was run in. The addition was completed in 20 minutes.

The flask was placed in a pan of water into which a slow stream of water was run for 2 days. The average temperature in the flask was about  $18^{\circ}\text{C}$ . The water was then turned off and the flask was left in the water bath for 5 more days, during which time the average temperature was about  $20^{\circ}\text{C}$ .

The batch was then mixed with 1000 ml. of water and steam distilled. The distillate measured 100 ml. and contained 28 ml. of tetranitromethane in the bottom layer. This was separated and washed: one wash with 60 ml.  $\text{H}_2\text{O}$ ; one wash with 60 ml. 0.25 Normal  $\text{Na}_2\text{CO}_3$ ; two washes with 60 ml.  $\text{H}_2\text{O}$ ; separated from water and shaken with 20 ml. concentrated  $\text{H}_2\text{SO}_4$ .

The tetranitromethane formed a layer on the top of the acid. It was almost colorless, having a very slight yellow tint. The yield was 46.2 g.; 47.2% of theory. The product froze at 14.2° to 14.0°C.

Potassium Salt of Nitroform  
by Ferrocyanide Reduction

Ten grams of tetranitromethane (f.p. 14.2° to 14.0°C.) was shaken with a solution of 50 g. of  $K_4Fe(CN)_6$  c.p. in 150 ml. of distilled  $H_2O$  at 20°C. The reaction was complete in 1 hr. The potassium salt of nitroform separated as bright yellow crystals. They were filtered, washed with a little ice water, sucked as dry as possible on a Buchner filter, and dried at room temperature. Yield 7.9 g.; 82.0% of theory.

Potassium Salt of Nitroform  
by Sodium Sulfite Reduction

Pure tetranitromethane weighing 19.6 g. was shaken with a solution of 14.0 g. of  $Na_2SO_3$  and 31 ml. of 2 molar KOH in 100 ml. of distilled  $H_2O$  at 40°C. Three additional portions of 31 ml. of 2 molar KOH were added at 10 min. intervals. After shaking for 45 min., a solution of 14.0 g. of  $Na_2SO_3$  in 100 c.c. of distilled water was added and the shaking continued for another 15 min. The batch was cooled in an ice bath and the yellow crystals of potassium nitroform were filtered off. The filtrate was treated with 50 g. of KCl and an additional crop of crystals was obtained:

Yield from original batch	10.6 grams
Yield from filtrate	5.3 grams
Total	15.9 grams

84.1% of theory



Preparation of a Solution of Nitroform  
in Carbon Tetrachloride

Dry HCl gas was bubbled through a suspension of 5.0 grams of dry potassium nitroform in carbon tetrachloride. After passing the HCl in for 10 minutes the yellow crystals had disappeared, leaving a pale yellowish-white residue. The CCl<sub>4</sub> layer was orange. It became colorless after standing for two days in a stoppered flask. The solid residue had a light blue-gray color. A small amount of the CCl<sub>4</sub> solution was shaken with water and the water was colored yellow.

No further work was done with this.

Preparation of Trinitroacetonitrile  
from Cyanoacetamide

To a mixture of 25 grams of red fuming nitric acid (d = 1.59) and 50 grams of concentrated sulfuric acid (96.3%), 8.4 grams of cyanoacetamide was added in small portions. The acid was mechanically stirred during the addition and the temperature was held below 20°C. by means of a water bath to which small pieces of ice were added as required. The addition of the cyanoacetamide was completed in 2 hrs. and 25 min. A gas was evolved during the addition and volatile white crystals were formed. The batch was stirred for 5 hrs. after the addition was complete. The temperature was constant at 12°C. during that time.

The flask was heated in a water bath at 55° to 60°. The crystals were sublimed and collected on a finger condenser cooled with ice water. The product was pure white. Yield 12.74 grams; 72.4% of theory.

Preparation of Trinitroacetonitrile  
from Cyanoacetic Acid

Cyanoacetic acid (90% pure) was added in small portions to a mixture of 25.0 grams of red fuming nitric acid ( $d = 1.59$ ) and 50.0 grams of concentrated sulfuric acid (98.3%). The mixed acid was stirred during the addition and the temperature was held below 22°C. by means of an ice water bath which was applied or removed as required. A total of 9.450 grams of the cyanoacetic, equivalent to 8.506 grams of 100% acid or 0.100 mole, was added during 1 hour and 50 minutes. A gas was evolved and a mass of white crystals formed in the flask.

The crystals were sublimed by heating the flask in a water bath at 55° to 60° C. and collecting the product on a finger condenser cooled with ice water. The sublimed material was pure white. Yield 7.92 grams; 45.0% of theory. The low yield in this experiment may have been due in part to loss by evaporation of some of the product.

Depression of the Freezing Point  
of Tetranitromethane

Chlorine:

A slow stream of chlorine gas from a cylinder was bubbled gently through 13.026 grams of tetranitromethane in a weighing bottle. The gas was passed in for 30 minutes, during which time the temperature rose from 27° to 28° C. and the weight increased by 0.305 gram. The solution was pale green in color. There was no evidence of chemical reaction.

After standing in the glass-stoppered weighing bottle at room temperature for three days, the sample weighed 36.602 grams and froze at 14.2° C. The green color had disappeared and the material was pure tetranitromethane. The maximum loss of tetranitromethane by evaporation was 0.093 gram.

The sample was cooled in an alcohol-dry ice bath and saturated with chlorine at -32° C. There were two phases, liquid and solid. The sample was allowed to warm until the crystals dissolved and the initial freezing point determined as 0° to -1° C.

Chlorine is not a suitable freezing point depressant, since its solubility at one atmosphere and room temperature is too low.

Nitrogen Peroxide:

Nitrogen peroxide was passed from a cylinder into a test tube, cooled in a beaker of cracked ice, until 1.4 grams

of the liquid had condensed. Tetranitromethane was added to bring the weight of the sample to 5.6 grams. This gave a 25% solution of nitrogen peroxide in tetranitromethane. The sample was cooled in an alcohol-dry ice bath until crystals formed and then warmed slowly in air until clear. The temperature at which the last crystals dissolved was  $-11.5^{\circ}\text{C}$ .

Nitrogen peroxide gas was passed into the sample cooled in an alcohol-dry ice bath until the nitrogen peroxide content was 1.7 grams or 28.8%. The initial freezing point of the solution was  $-21.5^{\circ}\text{C}$ .

After standing over night at room temperature, the freezing point was  $-16.3^{\circ}\text{C}$ .

Nitrogen peroxide can be used as a freezing point depressant if the solution is kept in closed tanks under slight pressure. A piece of aluminum foil has shown no sign of corrosion after six months' contact with the solution prepared in this experiment.

#### Acetic Acid:

A solution of 1.427 grams of glacial acetic acid in 12.838 grams of tetranitromethane was prepared. The solution contained 10% glacial acetic acid by weight. The initial freezing point of the solution was  $5.7^{\circ}\text{C}$ . This figure could not be used to determine the molal freezing point depression rate for tetranitromethane, since glacial acetic acid is not a pure compound and contains some associated molecules.

The solution did not explode under the impact of a 500 gram weight falling 100 centimeters.

Carbon Tetrachloride:

A solution of 1.538 grams of c.p. carbon tetrachloride in 10.000 grams of pure tetranitromethane, f.p., 14.2° C., was cooled in an ice water bath. The initial freezing point was determined as 4.2° C. Since the solution was molal in concentration, the molal freezing point depression rate for the tetranitromethane was determined as 10.0° C.

Sensitivity of Tetranitromethane  
to Heat and Shock

Heat Tests:

A steel plate 4" x 4" x 1/32" was heated in an air bath at 300° C. for 15 minutes. A drop of tetranitromethane was placed on the surface. There was no explosion or flash, but the substance bubbled and decomposed giving off NO<sub>2</sub>. The test was repeated nine times, with the same result. The plate was heated to redness and 10 drops of tetranitromethane were dropped on the surface, one at a time. The compound decomposed rapidly and formed NO<sub>2</sub> but there was no flash or explosion.

Samples of materials wet with tetranitromethane were placed on paper which was then ignited. The following results were obtained:

<u>Substance</u>	<u>Results</u>
Sawdust	Rapid burning, no explosion
Absorbent Cotton	Rapid burning, no explosion
Wood (pine)	Rapid burning, no explosion
Paper Towel	Rapid burning, no explosion

A closed 4 ounce screw-capped bottle containing 50 ml. of tetranitromethane was placed in a wood fire. The bottle burst and the fire burned brightly for a few seconds but there was no explosion.

Shock Tests:

Impact tests were made with a drop test apparatus using an 8 pound weight. The following comparisons were made with other explosives:

<u>Material</u>	<u>Drop in Inches</u>	<u>Result</u>
Tetranitromethane	24	No explosion
Sawdust wet with )	6	Explosion
tetranitromethane )	3	Partial explosion
	2	No explosion
Nitroglycerine	2*	Explosion
Textryl	5*	Explosion
RDX	4*	Explosion
TNP	15*	Explosion

\*Low sensitivity limit

A number 6 electric blasting cap was placed in 50 ml. of tetranitromethane in a 4 ounce glass bottle. The cap was exploded but the tetranitromethane did not detonate. There was no evidence of decomposition.

The following materials were wet with tetranitromethane, placed in cardboard mailing tubes, and initiated by number 6 electric blasting caps:

<u>Material</u>	<u>Quantity</u>	<u>Result</u>
Absorbent cotton	25 grams	Low order explosion, NO <sub>2</sub> fumes
Sawdust	25 grams	Violent detonation, bright flash, no smoke
Paper towels	3	Violent detonation, bright flash, no smoke

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