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By C. F. van Duin and B. C. Roeters van Lennep

Translated by Charles E. Munroe
Chairman, Committee on Explosives Investigations, Division of
Chemistry and Chemical Technology, National
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RESEARCHES ON MODERN BRISANT NITRO EXPLOSIVES*

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INTRODUCTION

In the examination of explosives there are actually established the following constants according to the methods developed by Bichel,[1] Kast,[2] Will, Dautriche, Noble, etc., and to the principles enunciated by Berthelot,[3] Sarrau, Vieille, Abel and others:

1. Velocity or rate of explosion
2. Energy liberated by the explosion
3. Composition of the products formed
4. Calculated temperature produced by the explosion
5. Pressure in a 15 l. Bichel[4] bomb
6. Enlargement of the cavity in a Trauzl lead block
7. Duration and length of the flame produced by the explosion of 100 g. of the substance
8. Stability and the initiating explosion temperature
9. Sensibility to shock

The greatest weight ought undoubtedly to be assigned to the constants 1, 2, 3, 8 and 9; but as we have not had at our disposal the necessary devices with which to measure the first three, we have

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* From *Recueil des Travaux Chimiques des Pays-Bas*, vol. 39, no. 2, pp. 145–177, Feb. 15, 1920.

[1] Bichel, "Methoden und Apparate der Sprengstoff A. G. Carbonit, zur Prüfung von Sprengstoffen."

[2] Kast, "Anleitung zur chemischen und physikalischen Untersuchung der Spreng- und Zündstoffe," Braunschweig, 1909.

[3] Berthelot, "Sur la force des matières explosives d'après la thermochimie," Paris, 1883.

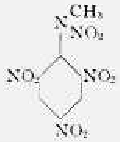
[4] Bichel, *Zeitschr. f. d. ges. Schiess- und Sprengstoffw.*, **3**, 365 (1901).

been limited to the determination of the stability and of the sensitiveness to shocks. The two last properties have had a special significance since Flürscheim[1] introduced into the technique of explosives substances having very mobile nitro groups, such as tetranitroaniline, while others have sought to employ the dinitramines.[2]

To render the researches on strongly nitrated compounds having one or more methylnitroamino groups or very mobile nitro groups as complete as possible, we have also sought to derive from the tetranitrophenylmethylnitramine, 2,4,6,2′,3′,4′-hexanitrodiphenylamine and tetranitrophenol some of those bodies which have not been employed as explosives because of their mode of preparation or their properties.

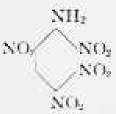
PREPARATION AND PROPERTIES

I. Tetranitrophenylmethylnitramine (Tetryl)



On the subject of this explosive one should consult existing works.[3]

II. 2,3,4,6-Tetranitroaniline



To the communications which we have already made[4] on the subject of the preparation and the properties of this compound, we now add the results of the study of the action of moist acetone upon it, in which we have identified the products formed in this reaction. By the action of moist acetone on the tetranitroaniline there are formed large quantities of hydrogen cyanide, together with the trinitroamidophenol previously mentioned. By distillation in a vacuum on the water bath, after having eliminated the acetone, there is obtained an acid liquid, which after neutralization with ammonia is colored black on warming after the addition of a silver salt.[5] We expected to find formic acid present, but have

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[1] D. R. P. 241,697 and 243,079.

[2] Brevet français, 391,107.

[3] Van Duin, *Rec. trav. chim.*, **37**, 111 (1917).

[4] Van Duin, *loc. cit.*, 111.

[5] This distillation ought to be conducted with great care, for there remains in the flask very impure trinitroamidophenol, which can give rise to an explosion. See the experience of Van Romburgh on the trinitromethylnitraminophenol. Van Romburgh, *Versl. Kon. Akad. van Wetensch. Amsterdam*, **23**, 1340 (1915).

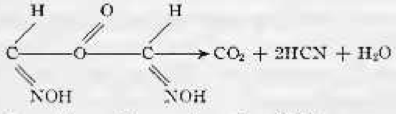
been unable to identify it in the products of the reaction. Apart from the water, which is a most important fraction, the distilled liquid appears to be composed as follows:

a. Formaldehyde.—This can be shown by a direct reduction of a solution of ammoniacal silver oxide and also of a dilute solution of potassium permanganate. It produced also an intense red color, characteristic of formaldehyde, when the liquid was mixed with a solution of 0.1 g. of morphine hydrochloride in 5 cc. of concentrated sulphuric acid.[1]

b. Acetic acid.—After neutralization with soda the liquid was evaporated and the salt obtained identified as sodium acetate, as follows: ferric chloride produced a red color and on boiling there was formed a precipitate of basic ferric acetate. On heating with alcohol and some drops of concentrated sulphuric acid, the odor of ethyl acetate was immediately perceived. On heating with a solution of *p*-nitrobenzyl bromide in 63% alcohol as indicated by Emmet Reid,[2] crystals were obtained which fused at 78°; when these were mixed with *p*-nitrobenzyl acetate, prepared according to the method described by the same author, there was no lowering of the melting point.

It was possible to show the presence of oxalic acid in the residue remaining in the flask. For this purpose the residue was extracted with hot water, neutralized by ammonia, and then acidified by acetic acid. On addition of a solution of calcium chloride there was observed the formation of a precipitate which immediately, when warm, reduced the solution of permanganate of potash slightly acidified by sulphuric acid. Thus products formed in the decomposition of aqueous solutions of di-isonitroso and isonitroso acetone were indicated, though we were not able to isolate them.

It is already known that when an aqueous solution of di-isonitroso acetone is heated, it decomposes as follows:



At the same time there is produced a little ammonia, hydrogen cyanide and oxalic acid:[3]

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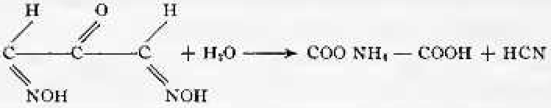
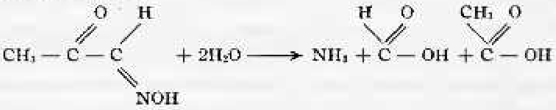
[1] Tendler and Manninck, *Zeitsch. f. anal. Chem.*, **48**, 310 (1909).

[2] Emmet Reid, *Journ. Amer. Chem. Soc.*, **39**, 124 (1917).

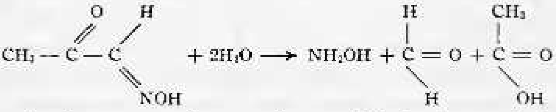
[3] Von Pechmann and Wehsarg, *Ber. d. deutsch. chem. Ges.*, **21**, 2989 (1888).



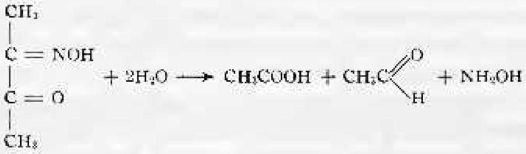
For the isonitroso acetone we have found that when this body is heated to 140° in the presence of dilute hydrochloric acid, it decomposes as follows:[1]



However, given the low temperature at which the action of moist acetone on tetranitroaniline occurs, the reaction can be accurately represented as follows:



This is why it appears, in accordance with the facts cited above, that the acid reaction of the distillate obtained by Van Romburgh, through the action of moist methyl ethyl ketone on tetranitrophenylmethylnitramine, should be attributed to the presence of acetic acid, and its reducing property to the presence of acetaldehyde. These compounds then appear to be produced from isonitrosomethylethylketone, as follows:



It may be considered established that Flürscheim was the first to knowingly prepare the tetranitroaniline. However, we believe that Witt and Witte[2] have had this substance in hand and have considered it as a trinitroaniline. These authors state that they obtained the 3,4-dinitroacetanilide,[3] melting point 144°, when a

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[1] Treadwell and Steiger, *Ber. d. deutsch. chem. Ges.*, **15**, 1059 (1882).

[2] Witt and Witte, *Ibid.*, **41**, 3005 (1908); see also Flürscheim, D. R. P. 243,079.

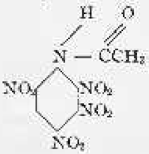
[3] Wender, *Gaz. chim. ital.*, **19**, 225 (1889).

solution of 10 parts of *m*-nitroacetanilide in 100 of 100% sulphuric acid was mixed below —5°, with a solution of 15 parts of dry potassium nitrate in 100 of 100% sulphuric acid and the whole allowed to remain at the ordinary temperature during 24 hours.

It is alleged that with longer standing there is formed, little by little, trinitroaniline. The authors have not given the fusion point or made other tests but they note that an analysis for nitrogen gave results corresponding with the calculated value for the trinitroaniline. If, however, we consider that the nitrogen contents of tri- and of tetranitroanilines differ but little (24.56% and 25.65%) one may realize that an examination of impure tetranitroaniline could lead one to believe it to have the composition of the trinitro product.

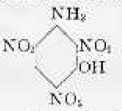
We have sought to prepare the trinitroaniline by the method described by Witt and Witte and, while we have carefully endeavored to follow the instructions given, we have never obtained trinitroaniline but always the tetranitro compound. This was identified not only by the fact that it had the same melting point and that when mixed with this substance the melting point was not lowered, but also because on boiling in the presence of moist acetone it gave 2,4,6-trinitroamidophenol. It may also be remarked here that by this process a very pure tetranitroaniline is immediately obtained.

III. Acetyltetranitroaniline



We prepared this body according to Flürscheim[1] by heating pure tetranitroaniline with acetic anhydride and a little sulphuric acid at a temperature not above 80°. After crystallization in glacial acetic acid the tetranitroaniline fuses, with decomposition, at 169–170°, cor.

IV. 2,4,6-Trinitroamidophenol



[1] Flürscheim, D. R. P. 241,697, *Chem. Zentr. Bl.*, **1**, 184 (1912); see also Witt and Witte, *oc. cit.*, for the preparation of acetylpicramide.