

By the prolonged action of bromine and nitric acid on mesitylene, tribromo-mesitylene is the chief product.

7.5 cc. of mesitylene are treated with 3 cc. of nitric acid and 6 cc. of bromine. The reaction starts at once and it is continued on a sand bath for three hours; bromine and nitric acid are added gradually in small portions at a time. A semisolid mass is obtained which is warmed on a basin with water to drive off the volatile matter. The product solidifies on cooling and consists of practically pure tribromo-mesitylene. The product on washing with benzene leaves behind white, silky crystals which are found to be pure tribromo-mesitylene, melting at 222–223°. The yield obtained is 5.5 g. of tribromo-mesitylene, or 33% of the theory.

Calc., Br = 67.22. Found, Br = 66.83.

**Ethyl Benzene.**—Ethyl benzene gives on short bromination with bromine and nitric acid, a mixture of *o*- and *p*-bromoethyl-benzene. For its preparation, 7 cc. of ethyl benzene are treated with 3 cc. of nitric acid and 4 cc. of bromine. The reaction begins at once with the evolution of nitrous fumes and generally the reaction becomes complete even without warming. The resulting product is washed, dried and distilled. After the passing out of unchanged ethyl benzene, the greater part boiled between 202–204°, which is a mixture of *o*-bromoethyl-benzene and *p*-bromoethyl-benzene. The yield obtained is 6 g., or 55% of theory.

Calc., Br = 43.24. Found, Br = 42.11.

After the distillation, a charred residue is left behind in the flask which is a mixture of higher bromo-derivatives of ethyl benzene.

Investigations on similar lines are being continued.

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[CONTRIBUTION FROM THE EXPLOSIVES LABORATORY OF THE BUREAU OF MINES, DEPARTMENT OF THE INTERIOR.]

## APPLICATION OF THE NITROMETER FOR THE DETERMINATION OF CONSTITUTION AND ESTIMATION OF NITROGEN IN A CLASS OF NITROCOMPOUNDS. (NITROAMINES).<sup>1</sup>

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The nitrometer reaction was first noted by Crum<sup>2</sup> in 1847; but it was not until 1878 when Lunge<sup>3</sup> succeeded in developing a practical instrument which he called the "nitrometer" that this reaction came into general use. Undoubtedly the most common application of the nitrometer is for

<sup>1</sup> Published by permission of Director, Bureau of Mines.

<sup>2</sup> *Phil. Mag.*, [3] 30, 426 (1847).

<sup>3</sup> *Ber.*, 11, 436; *Chem. News*, 38, 18 (1878); *Dingler's Polytech. J.*, 228, 448 (1878).

the estimation of nitrogen as nitric oxide (NO) in nitric and nitrous acids their salts and esters. However, the nitrometer is by no means limited to these reactions.

In the literature may be found applications of the nitrometer for analyses of a great variety of compounds. According to Lunge<sup>1</sup> it may be employed in general for all analytical operations in which a definite quantity of gas is evolved, not soluble to a very considerable extent in the liquid from which it is evolved, and not acting upon mercury. He employs the nitrometer for determining the strength of standard acids, by introducing into the nitrometer a measured volume of the acid with an excess of sodium or calcium carbonate and measuring the volume of CO<sub>2</sub> liberated. From this the strength of the acid may be calculated. By using a weighed quantity of carbonate and an excess of acid the carbonate may be determined. The strength of hydrogen peroxide may be determined by measuring the volume of oxygen evolved by the action of bleaching powder and *vice versa*. Potassium ferricyanide in alkaline solution liberates oxygen from hydrogen peroxide and may be analyzed in like manner. Lunge also employed the nitrometer for estimating indigotin in reducing solutions of indigo, by means of absorption of oxygen. For a further list of methods and of the varied application of the nitrometer, Warrington,<sup>2</sup> Allen<sup>3</sup> and Baumann<sup>4</sup> should be consulted.

The fact that in the nitrometer it is possible to obtain the nitrogen as NO from nitric and nitrous esters and not from most characteristic nitrocompounds has long been used as a means of distinguishing the respective esters from nitrocompounds. A statement to this effect was made by Lunge<sup>5</sup> as follows:

"I have also made experiments to determine whether characteristic nitrobodies will liberate nitric oxide as do the nitric esters by shaking with sulfuric acid and mercury. Although not apparent it would not seem impossible, that under these conditions sulfonic acids form and the feed nitric acid would react upon mercury, *e. g.*,  $C_6H_5NO_2 + SO_4H_2 = C_6H_5SO_3H + NO_3H$ . But nitrobenzol with sulfuric acid on the most vigorous shaking in the nitrometer gave no trace of gas, and furthermore remained unchanged. One may, therefore, safely conclude that the characteristic nitrobodies have this distinction from the nitric esters of glycerin, cellulose, and other analogous compounds."

As further evidence of the stability of characteristic compounds toward the nitrometer reaction the following nitrocompounds were investigated in this laboratory: Nitromethane, CH<sub>3</sub>.NO<sub>2</sub>; dinitrobenzene, *o*-, *m*- and *p*-C<sub>6</sub>H<sub>4</sub> : (NO<sub>2</sub>)<sub>2</sub>; dinitrophenol, 1 : 2 : 4, C<sub>6</sub>H<sub>3</sub>(OH) : (NO<sub>2</sub>)<sub>2</sub>; dinitronaphthalene, 1 : 8, C<sub>10</sub>H<sub>6</sub> : (NO<sub>2</sub>)<sub>2</sub>; trinitrotoluene, 1 : 2 : 4 : 6,

<sup>1</sup> *J. Soc. Chem. Ind.*, 4, 447 (1885).

<sup>2</sup> *J. Chem. Soc.*, 35, 375 (1879).

<sup>3</sup> *J. Soc. Chem. Ind.*, 4, 178 (1885).

<sup>4</sup> *Z. angew. Chem.*, 4, 135, 203, 328, 339, 392, 450 (1891).

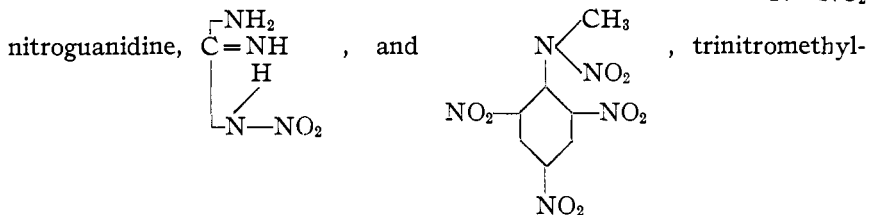
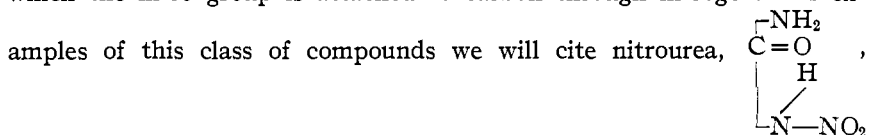
<sup>5</sup> *Dingler's Polytechnic. J.*, 245, 171 (1882).

$C_6H_2.(CH_3)_3 : (NO_2)_3$ ; and tetranitroaniline, 1 : 2 : 3 : 4 : 6,  $C_6H_4.(NH_2) : (NO_2)_4$ .

In no case with any of the above nitrocompounds could any gas be detected in the nitrometer on the most vigorous shaking with sulfuric acid and mercury. In all the above compounds it should be noted that the nitrogen of the nitro group is attached directly to the carbon atom.

In summarizing other reactions which identify characteristic nitrocompounds and nitrous and nitric esters we find the lines rather sharply drawn. The esters are more or less readily saponified by caustic potash into alcohols and the respective salts. Nitrocompounds are not saponifiable. When caustic potash reacts upon these, the products of reaction are not alcohols and nitrites or nitrates. By reduction the esters are converted into alcohol and ammonia, while the nitrocompounds under similar conditions yield as final products aminocompounds. The acid character of the aliphatic nitrocompounds is shown by the fact that one hydrogen atom attached to the same carbon atom as the nitro group is readily replaced by a metal. This cannot apply to the aromatic compounds, since the nitro group is attached to a tertiary carbon atom.

We will now turn to a class of nitrocompounds, the nitroamines, in which the nitro group is attached to carbon through nitrogen. As examples of this class of compounds we will cite nitrourea,



nitramine, usually called tetranitromethylaniline and known commercially as "tetryl."

In spite of the strongly basic character of guanidine, nitroguanidine<sup>1</sup> is a feebly acid substance. When boiled with caustic potash,  $CO_2$ ,  $N_2O$  and ammonia are formed. With zinc dust and acetic acid nitrosoguanidine and then aminoguanidine are formed. By treating with a hydrochloric acid solution of stannous chloride, ammonia and guanidine are formed.

Nitro urea is a strong acid;<sup>2</sup> its alkali salts are neutral in reaction and it expels acetic acid from acetates. From this reaction it should be con-

<sup>1</sup> *Beilstein*, Vol. I, 1163.

<sup>2</sup> Richter's "Organic Chemistry" (Spielman), I, p. 441.

sidered an iso-nitrocompound, 
$$\begin{array}{c} \text{N}=\text{N}=\text{O} \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{OH} \\ | \\ \text{C}=\text{O} \\ | \\ \text{NH}_2 \end{array}$$
 On reduction it gives first

nitroso and then aminourea.

Trinitromethylnitramine undoubtedly also gives all the characteristic reactions of true nitrocompounds. This compound is of particular interest because it has three nitro groups attached directly to the carbons in the ring and one nitro group linked to carbon through a secondary nitrogen.

The nitroamines described were selected at random as types of nitrocompounds in which the nitro group is attached to carbon through nitrogen. The reactions indicated show them to respond to most reactions for true nitrocompounds. When subjected to the nitrometer reaction they yielded only the nitrogen of the nitro group attached to carbon through nitrogen. In this reaction they behave like the nitric and nitrous esters.

The du Pont<sup>1</sup> modification of the Lunge nitrometer and the decomposition flask method of Berl and Jurrissen<sup>2</sup> were used in the determination of nitrogen. The decomposition flask method of Berl and Jurrissen is not known generally in this country and, therefore, a short description of the apparatus and method of operation will be appropriate. The apparatus consists of a heavy-walled round-bottom flask of 300 cc. capacity, with a ground-in bulb-shaped glass fitting. The fitting is composed of two parts: a 50 cc. tap funnel through the side of the bulb, with its stem extending below the neck of the flask; and an exit tube, containing a two-way stop-cock, in the top of the bulb. The fittings and cocks are all greased with a mixture of vaseline and caoutchouc.

The substance to be analyzed is placed in the flask, which is then closed with the fitting. The flask is evacuated through the exit tube and CO<sub>2</sub> introduced. This operation is repeated three times and the flask is finally again exhausted. About 20 cc. conc. H<sub>2</sub>SO<sub>4</sub> are added through the tap funnel, and the flask is shaken until the substance dissolves. Ten to fifteen grams of mercury are then added through the funnel and the flask shaken until NO is completely evolved.

The success of this method depends principally upon good fittings and pure CO<sub>2</sub>. By using a CO<sub>2</sub> generator similar to the one described by Young and Caudwell<sup>3</sup> and developed by one of us<sup>4</sup> in this laboratory, no difficulty was experienced in obtaining a supply of pure CO<sub>2</sub>. The gas generated in the flask is displaced by the rapid introduction of a saturated solution

<sup>1</sup> *J. Soc. Chem. Ind.*, **19**, 982 (1900).

<sup>2</sup> *Z. angew. Chem.*, **23**, 241 (1910).

<sup>3</sup> *J. Soc. Chem. Ind.*, **26**, 184 (1907).

<sup>4</sup> "Determination of Nitrogen in Substances Used in Explosives," Bur. Mines, *Tech. Paper* 160.

of sodium sulfate through the funnel and is collected in a buret over mercury. The volume is observed, the gas run into a caustic potash solution, returned to the buret and the reading taken. The quantity of  $\text{CO}_2$  absorbed varies from two to three cubic centimeters. The gas is then passed into a pipet containing a saturated solution of ferrous sulfate and well shaken. The residual gas is then returned to the buret and the reading observed. The residual gas varies from 1.5 to 2.0 cc. In treating a sample of gas obtained in the nitrometer from  $\text{KNO}_3$  in above manner it was found that a 100 cc. sample left a residue of 1.7 cc. It was consequently considered permissible to add this residual gas to the  $\text{NO}$  absorbed by ferrous sulfate. From this volume, after reducing to standard conditions, the percentage of nitrogen was calculated.

Representative samples of gas from each of the compounds analyzed in the du Pont nitrometer were passed into  $\text{FeSO}_4$  solution and in all cases gave results that left no doubt that the gas consisted entirely of nitric oxide.

TABLE OF NITROGEN DETERMINATIONS.

Substance.	Grams taken.	Method.	Percentage of N found.	Theory.
Nitrourea.....	1.0000	Nitrometer	13.17	13.33
Nitrourea.....	1.0000	Nitrometer	13.20	
Nitroguanidine....	1.0000	Nitrometer	13.32	13.46
Nitroguanidine....	0.3030	B. & J. (a)	13.54	
Nitroguanidine....	0.3580	B. & J. (a)	13.42	
Tetryl.....	2.5000 (b)	Nitrometer	4.71	4.88
Tetryl.....	2.5000 (b)	Nitrometer	4.74	
Tetryl.....	2.5000 (c)	Nitrometer	4.71	
Tetryl.....	2.5000 (c)	Nitrometer	4.74	
Tetryl.....	0.9000 (c)	B. & J. (a)	4.87	
Tetryl.....	0.9000 (c)	B. & J. (a)	4.90	

(a) = Berl and Jurrissen method.

(b) = Commercial tetryl.

(c) = Tetryl crystallized from benzene.

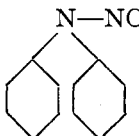
### Observations on Results.

The nitrometer results are consistently somewhat low. This is due to a slight action of the sulfuric acid on these nitrocompounds and consequent loss of a small amount of gas, before forcing the substance into the nitrometer bulb. The results with the decomposition flask are all well within experimental error.

The nitrometer and especially the decomposition flask method of Berl and Jurrissen are well adapted for the determination of nitrogen in nitrocompounds where the nitro group is attached to the carbon through a nitrogen atom.<sup>1</sup>

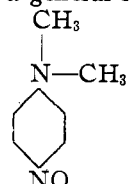
<sup>1</sup> It is, perhaps, of interest to note that these compounds may be considered as esters of nitric acid,  $\text{NO}_2\text{—O—R}$  in which the oxygen atom connecting R with  $\text{NO}_2$  is replaced by NH. It recalls the work of E. C. Franklin who has shown that  $\text{K—NH—H}$  is base and acetamide,  $\text{C}_2\text{H}_3\text{O—NH—H}$  is an acid in anhydrous ammonia.—EDITOR

In the nitric esters we have  $\equiv\text{C}-\text{O}-\text{NO}_2$ , or the  $\text{NO}_2$  group linked to carbon through an oxygen atom. In the nitrocompounds under discussion,  $\equiv\text{C}-\text{N}\begin{cases} \text{H or CH}_3 \\ \text{NO}_2 \end{cases}$ , the nitro group is linked to carbon through a nitrogen atom. If we now turn to the nitrous esters  $\equiv\text{C}-\text{O}-\text{NO}$  we find an  $\text{NO}$  group linked to carbon through oxygen. By analogy we should expect nitroso compounds in which the nitroso group is linked to carbon through nitrogen likewise to yield its nitroso nitrogen in the nitrometer reaction.

Nitroso diphenylamine, , was selected as a compound of

this type. As sulfuric acid causes a rather violent reaction upon this substance the decomposition flask was used for this reaction. The results obtained were 6.97, 6.94, and 7.05% N, theoretical 7.07% N. Again allowing for impurities in the sample, these results are well within experimental error. The gas formed was examined in the same manner as in previous experiments, and was identified as nitric oxide.

To allay any apprehension that this might be a general reaction for all

nitroso compounds, *p*-nitrosodimethylaniline, , was selected

as one which had the nitroso group attached directly to carbon. Sulfuric acid likewise acts rather violently on this substance, but on completing the reaction with mercury, about one-sixth the theoretical quantity of gas was formed, and only a trace of this was absorbed by ferrous sulfate solution. This also shows that the nitroso group must be attached to the carbon atom through nitrogen, in order that the nitroso nitrogen may be determined by the nitrometer reaction.

A curious anomaly occurs when it is attempted to determine nitrogen in urea and guanidine nitrates in the nitrometer in the usual manner, *i. e.*, by dissolving in a small quantity of water, introducing into bulb, then adding the sulfuric acid, etc. Results were obtained varying from 13.3 to 15.6% N if all the gas formed is considered as  $\text{NO}$ . This was not the case, as on a few qualitative tests the gas showed considerable  $\text{CO}_2$  and  $\text{N}_2$  besides the  $\text{NO}$ . Theoretical nitrate nitrogen for urea nitrate is 11.38% and for guanidine nitrate 11.48%. Both these compounds must first be converted into their respective nitrocompounds before they can

be determined in the nitrometer. This is easily accomplished by slowly adding a weighed sample (*e. g.*, 1 g.) of the nitrate to 20 cc. conc. sulfuric acid cooled to 0° and kept at this temperature until all the nitrate is dissolved. This converts the nitrate into the nitrocompound, which may then be introduced into the nitrometer, the cup washed with 10 cc. additional sulfuric acid, and the reaction completed in the usual manner. This method will yield practically theoretical results for the nitrates.

#### Summary.

1. The nitrometer has been used for a great variety of analytical operations, in which a definite quantity of a gas is evolved, not soluble to a very considerable extent in the liquid from which it is evolved, and not acting upon mercury.

2. The characteristic nitrometer reaction has been used only for nitrous and nitric acid, their salts and esters.

3. Further evidence is given that the nitrometer reaction does not liberate NO from true nitrocompounds in which the nitro group is linked directly to the carbon atom.

4. Characteristic reactions for nitrocompounds are given and evidence is produced that nitrocompounds in which the nitro group is attached to carbon through nitrogen give most of these reactions.

5. The application of the true nitrometer reaction is extended for the determination of nitrogen of the NO<sub>2</sub> and NO groups in nitroamines and nitrosoamines in which the respective groups are attached to carbon through nitrogen.

6. The nitrometer reaction may be used as a means of ascertaining whether the NO<sub>2</sub> and NO group is attached directly to the carbon or through a nitrogen atom.

7. An anomaly is noted in which the nitrates of urea and guanidine cannot be determined in the nitrometer in the usual manner. They must be converted into their respective nitrocompounds first, after which they may be readily determined.

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### THE COMPOSITION OF NEUROKERATIN.

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Neurokeratin, which was first isolated by Kühne, is supposed to be the chief characteristic constituent of the neuroglia cells of the brain, and of the axilemma and outer sheath of the medullary substance of the nerve trunks. It is classed chemically with the general group of keratins,