

the reaction is complete the solution is filtered through a little glass wool to remove the excess of magnesium and allowed to flow into a test-tube containing about 4.5–5.0 g. of mercuric bromide or iodide, depending on the halogen in the original alkyl halide. The reaction mixture is warmed and shaken for a few minutes and then evaporated to dryness. The residue is boiled with about 20 cc. of 95% alcohol and the solution is filtered, diluted with 10 cc. of water and cooled. The alkyl mercuric halide separates in beautiful crystals, one crystallization usually giving a sharply melting product.

Runs with greater quantities were also made in order to obtain enough of the various derivatives for determination of melting points and analysis. The new compounds that have been prepared are given in Table II.

TABLE II
NEW ALKYL MERCURIC HALIDES

	M. p., ° C. (corr.)	Formula	Analysis	
			Calcd., %	Found, %
Mercuric bromide				
Ethyl.....	193.5	C ₂ H ₅ HgBr	C, 7.76	7.72
<i>n</i> -Propyl.....	138	C ₃ H ₇ HgBr	C, 11.12	11.18
<i>iso</i> Butyl.....	55.5	C ₄ H ₉ HgBr	Hg, 59.46	59.1
<i>n</i> -Amyl.....	122	C ₅ H ₁₁ HgBr	Hg, 57.05	56.80
<i>n</i> -Hexyl.....	118.5	C ₆ H ₁₃ HgBr	Hg, 54.86	54.36
<i>n</i> -Heptyl.....	114.5	C ₇ H ₁₅ HgBr	Hg, 52.58	52.21
<i>n</i> -Octyl.....	109	C ₈ H ₁₇ HgBr	Hg, 50.96	50.72
Mercuric iodide				
<i>n</i> -Propyl.....	112.5	C ₃ H ₇ HgI	C, 9.72	9.69
<i>n</i> -Butyl.....	117	C ₄ H ₉ HgI	C, 12.48	12.59
<i>iso</i> Butyl.....	72	C ₄ H ₉ HgI	C, 12.48	Not analyzed

Summary

Primary alkyl bromides and iodides are easily converted into the corresponding mercuric halides, which are suitable derivatives for identification.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

NITROGEN TETROXIDE AS A REAGENT FOR DIAZOTIZATION

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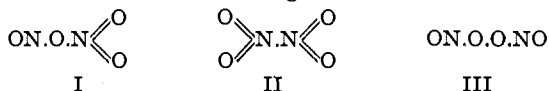
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The object of this research, the results of which are recorded in this paper, was to demonstrate experimentally that the diazotization of a primary aromatic amine can be accomplished successfully by allowing the base to interact with pure nitrogen tetroxide, N₂O₄, in an anhydrous solvent at ordinary temperature. This reaction has now been applied

¹ Constructed from a dissertation presented by Bruce Houston to the Faculty of the Graduate School of Yale University, June, 1923, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

with success to the diazotization of the three amines, *o*-, *m*- and *p*-nitro-aniline, and the method should prove of practical utility in special cases where it is desirable or necessary to bring about diazotization in a neutral organic solvent. This characteristic behavior of nitrogen tetroxide towards amines demands, therefore, the adoption of an acceptable structural formula for this reagent to enable us to interpret satisfactorily the mechanism of the reaction. Of the three structural formulas that have been proposed by different workers for this oxide, the data presented in this paper seem to show that Formula I is the only one that satisfies the requirement of our reaction. In other words, the action of nitrogen tetroxide on an aromatic amine is to be expressed in general as follows: $C_6H_5NH_2 + ON.O.NO_2 = C_6H_5N:N.ONO_2$ (diazobenzene nitrate) + H_2O .

The three structural formulas I, II, III, which have been proposed to represent the constitution of nitrogen tetroxide have all been actively



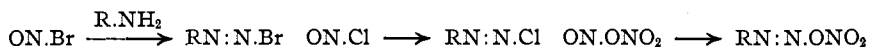
supported by different investigators. Since, however, it is not our purpose to discuss in this paper the general question of tetroxide structure and the evidence hitherto brought forward in support of each of these proposed formulas, we shall confine ourselves strictly to the reaction under discussion, and to the evidence in support of the nitrosyl nitrate structure I for nitrogen tetroxide.

That nitrogen tetroxide reacts at a low temperature and in an anhydrous solvent with a primary amine as a diazotizing agent was apparently first observed by O. N. Witt² whose work on this subject is published in an obscure journal. Witt allowed the anhydrous oxide to interact with aniline in benzene and obtained a quantitative yield of benzene diazonium nitrate which he identified as an azo compound after coupling with *p*-phenylenediamine. He made no mention of the formation of diazo-amidobenzene in his work and the change, therefore, may be expressed according to the equation given above. It is quite remarkable that this early work of Witt has apparently never received any attention. A search of the available literature on nitrogen tetroxide has revealed only one reference to the application of this reaction.

In our work with the three isomeric nitro-anilines, we have observed in every case the formation of a diazo-amidobenzene derivative as well as the corresponding diazonium nitrate by the action of nitrogen tetroxide on these amines. The relative amounts of the two compounds formed are dependent upon the molecular proportion of the oxide used in the reaction. The results obtained by us in our research not only confirm the

² Witt, *Tagebl. Natf.-Vers. Baden-Baden*, 194 (1879); *Chem. Zentr.*, **11**, 226 (1880).

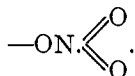
early observation of Witt, but also contribute further evidence in favor of the nitrosyl nitrate structure for nitrogen tetroxide. In other words, nitrogen tetroxide, nitrosyl bromide and nitrosyl chloride are representatives of the same type of compound, being nitroso derivatives of the corresponding monobasic acids, and the behavior of the three reagents towards primary amines may be expressed as reactions of the same general type,³ leading to the formation of diazonium salts. The more recent



observations reported by Schaarschmidt and his co-workers⁴ on the behavior of nitrogen tetroxide and nitrosyl chloride towards benzene in the Friedel and Crafts reaction also indicate the analogy in structure of these two nitrogen compounds.

That the nitrosyl-nitrate formula I expresses satisfactorily the constitution of the endothermic compound (liquid nitrogen tetroxide) is supported further by the experimental data, which have been revealed by previous workers as a result of the study of the following six specific reactions.

1. The interaction of alkyl halides with nitrogen tetroxide with formation of alkyl nitrates, which was studied by Henry,⁵ in 1874. This investigator pointed out the difficulty of reconciling such a behavior with Formula II; nor would the action observed be explicable by the peroxide structure III, since it would be expected from our knowledge of peroxide linkages that the bond between the two oxygens would be the first to break in any reaction of a combination having this constitution. To explain the formation of alkyl nitrates by the aid of Formula III, it would be necessary to assume first a breaking of a bond between nitrogen and a peroxide-oxygen —O.O, to be followed by a subsequent rearrangement of the nucleus —O.ONO to a nitrate ion containing pentavalent nitrogen,



2. The interaction of potassium nitrate, sodium chloride and sodium bromide with nitrosyl sulfuric acid which Gerard and Pabst⁶ have shown to react with production of nitrogen tetroxide, nitrosyl chloride and nitrosyl bromide, respectively. $\text{HO.SO}_2\text{O.NO} + \text{KO.NO}_2 = \text{HO.SO}_2\text{OK} + \text{ON.ONO}_2$.

3. The action of nitrogen tetroxide on monomethylaniline which

³ Spielmann, "Richter's Organic Chemistry," vol. 1, P. Blakiston's Son and Co., Philadelphia, p. 162. Kastle and Keiser, *Am. Chem. J.*, **17**, 91 (1895).

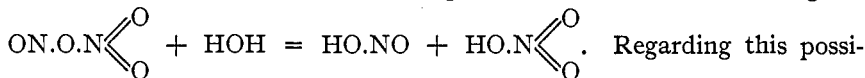
⁴ Schaarschmidt, *Ber.*, **57**, 2065 (1924). Schaarschmidt and Raeck, *Ber.*, **58**, 349 (1925).

⁵ Henry, *Bull. sci. acad. roy. belg.*, [2] **38**, 1 (1874).

⁶ Gerard and Pabst, *Bull. soc. chim.*, [2] **30**, 531 (1878).

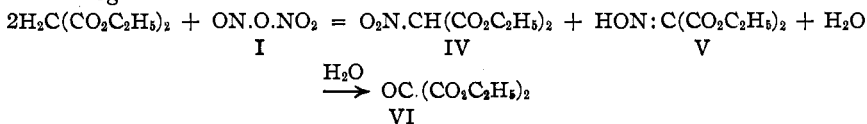
gives, according to Stoermer,⁷ *p*-nitronitrosomethylaniline. $\text{CH}_3\text{NH}\cdot\text{C}_6\text{H}_5 + \text{ON}\cdot\text{ONO}_2 = \text{CH}_3(\text{NO})\text{N}\cdot\text{C}_6\text{H}_4\text{NO}_2 + \text{H}_2\text{O}$.

4. The characteristic behavior of nitrogen tetroxide towards water when the two products of reaction are nitrous and nitric acids. These acids contain nitrogen atoms of different valences; hence, it must be that these two atoms are of dissimilar valence in the original molecule as expressed in the equation below, otherwise it must be supposed that mutual-oxidation and reduction have taken place between these two nitrogens.



bility of mutual oxidation and reduction it is to be noted that in Formula II both nitrogens are assigned a valence of five while in the alternative formula, III, both are assigned a valence of three. Hence, in either of these cases, one atom would have to retain its original valence and the other change, a conception which is hardly in accord with our present views of oxidation and reduction.

5. The characteristic behavior of nitrogen tetroxide when allowed to interact with dimethyl or diethyl malonate. Bouveault and Wahl⁸ have shown that the two primary products of reaction in this case are ethyl nitromalonate, IV, and the corresponding isonitroso ester, V. In other words, nitrogen tetroxide serves as a reagent for converting diethyl malonate into diethyl oxomalonate, VI. The primary reaction is satisfactorily explained by assuming the nitrosyl nitrate structure I for nitrogen tetroxide.



6. Finally the unique behavior of nitrogen tetroxide towards mercury diphenyl, which is easily explained as expressed below, by use of the nitrosyl-nitrate structure I.⁹ $\text{Hg}(\text{C}_6\text{H}_5)_2 + \text{ON}\cdot\text{O}\cdot\text{NO}_2 = \text{C}_6\text{H}_5\text{NO} + \text{Hg}(\text{C}_6\text{H}_5)\text{O}\cdot\text{NO}_2$.

Experimental Part

The Action of Nitrogen Tetroxide on *m*-Nitro-aniline and the Formation of 3,3'-Dinitrodiazo-amidobenzene, $\text{NO}_2\text{C}_6\text{H}_4\text{N}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{NO}_2$.—Pure, anhydrous nitrogen tetroxide was prepared according to the method of Cundall,¹⁰ which is based on the reaction between the proper proportions of a mixture of fuming nitric and concd. sulfuric acids with arsenic trioxide. The gas produced by this reaction was thoroughly dried by passage through a series of drying tubes containing phosphorus pentoxide and finally

⁷ Stoermer, *Ber.*, **31**, 2525 (1898).

⁸ Bouveault and Wahl, *Compt. rend.*, **137**, 196 (1903).

⁹ Bamberger, *Ber.*, **30**, 507 (1897).

¹⁰ Cundall, *J. Chem. Soc.*, **59**, 1077 (1891).

condensed to a liquid. To purify the oxide further it was then fractionally distilled through a tower containing phosphorus pentoxide, the middle fraction being saved and preserved in liquid form out of contact with the air.¹¹ A description of one experiment will serve to show our method of utilizing this oxide as a diazotizing agent.

Twenty-five g. of *m*-nitro-aniline was dissolved in 1800 cc. of benzene which had previously been thoroughly dried by digesting with finely divided sodium, and the pure nitrogen tetroxide, in vapor form, allowed to float over the surface of the benzene solution. The latter was thoroughly stirred during the operation and also kept cold and protected from the air. The oxide dissolved immediately and the treatment was continued until the benzene solution had assumed a distinct and permanent reddish color, indicating an excess of the gas. The reaction was almost instantaneous when the nitrogen tetroxide dissolved in the cold benzene solution, and a pale yellow, crystalline substance began to separate at once. On continued absorption of gas, this precipitate finally assumed a coagulated condition somewhat gummy in consistency and when nitrogen tetroxide was passed into the solution in excess the reaction fluid became green. When the treatment was stopped as soon as all visible precipitation ceased, an excellent yield of a light colored powder was obtained. In fact, the interaction with *m*-nitro-aniline is so complete that the base can be removed almost completely from the benzene solution. This compound was found to be insoluble in benzene, ether, ethyl acetate and chloroform. When warmed with glacial acetic acid or with alcohol it was observed to undergo decomposition slowly. It was purified by crystallization from acetone and separated from this solvent in the form of yellow, fibrous needles matted together; m. p., 195–196° with violent decomposition. The compound was identified by analysis, molecular-weight determination, and chemical behavior as 3,3'-dinitrodiazo-amidobenzene.

Anal. Calcd. for $C_{12}H_9O_4N_5$: C, 50.2; H, 3.1; N, 24.40. Found: C, 50.7; H, 3.3; N, 24.24.

Mol. wt. (ebullioscopic method, using acetone as the solvent). Calcd. for $C_{12}H_9O_4N_5$: mol. wt., 287. Found: 282.

Preparation of the Diazo-amido Compound for Comparison with our Product by the Method of Meldola and Streatfeild.¹²—The *m*-nitro-aniline was diazotized in aqueous hydrochloric acid solution and the diazo-amido derivative filtered off and purified by crystallization from alcohol. It separated from this solvent or acetone in the form of pale yellow needles; m. p., 194–196° with intense decomposition. The compound agreed in all its properties with the compound obtained by the action of nitrogen tetroxide on *m*-nitro-aniline and a mixture of the two compounds melted sharply at 195–196°.

A Quantitative Study of the Reactions between Nitrogen Tetroxide and the Three Isomeric Nitro-anilines.—The apparatus used in these experiments consisted of a small glass bulb A into which two tubes fitted with stopcocks were sealed, and a gas wash bottle to which had been sealed two stopcocks. Pure, anhydrous nitrogen tetroxide was condensed in the bulb A and its weight accurately determined. Then an anhydrous benzene solution of the nitro-aniline under investigation was introduced into a wash bottle B, the amount of amine taken being determined by the weight of the tetroxide condensed in A and the molecular proportions desired for the experiment. The bulb A and receiver B were then connected

¹¹ It was our experience that nitrogen tetroxide furnished in cylinders by the U. S. Army Ordnance Dept. was of a high degree of purity, and when purified according to our method served satisfactorily for large unit operations.

¹² Meldola and Streatfeild, *J. Chem. Soc.*, 51, 102 (1887).

and the nitrogen tetroxide was slowly distilled into the cold solution of the amine while the latter was constantly shaken to hasten solution. The last traces of nitrogen tetroxide in A were forced into B by means of a current of carbon dioxide. As the diazonium nitrates produced from the respective amines used were found to be formed in greater or less proportions along with the corresponding diazo-amidobenzenes, and as these diazonium salts are extremely soluble in water, a separation of the two compounds was easily accomplished. The precipitate of the diazo-amido compound formed was first separated by filtration and the benzene solution then shaken with about 200 cc. of cold water. In this manner a water solution of the diazonium salt could easily be obtained and the diazo-amido derivative collected on a filter. Our method of identifying and measuring the quantity of diazonium salt present in aqueous solution was by coupling with β -naphthol in alkaline solution to form an insoluble azo dye. These dyes have all been described and hence were readily identified. The diazo-amido compound was weighed after being thoroughly dried in a vacuum over sulfuric acid. The nitro-anilines were all carefully purified by recrystallization and their melting points accurately established. Benzene was the solvent employed in all of our experiments and was carefully dried before being used by long digestion with sodium in wire form.

Experiments with *m*-Nitro-aniline.—It was found that the reaction could be varied by changing the molecular fractions of the reacting constituents so that the yields of 3,3'-dinitrodiazo-amidobenzene varied between 97 and 24%, calculated on the basis of the quantity of nitro-aniline used, while at the same time the diazonium nitrate yield rose from 2 to 69%. The azo dye obtained by coupling with β -naphthol, $\text{NO}_2\text{-C}_6\text{H}_4\text{.N:N.C}_{10}\text{H}_6\text{OH}$, was shown to be identical with the compound prepared for identification by Meldola's method¹³ and crystallized from toluene in the form of orange plates having a metallic luster; m. p., 191–192°. The results of four experiments are recorded in Table I.

TABLE I
DIAZOTIZATION OF *m*-NITRO-ANILINE WITH NITROGEN TETROXIDE

N_2O_4 , g.	<i>m</i> -Nitro-aniline, g.	Ratio of N_2O_4 /to base	Diazo-amino compound		Azo dye, g.	Yield of diazonium nitrate, %
			G.	%		
2.117	6.34	1:2	6.3	97	0.25	2.0
2.84	4.26	1:1	1.45	33	3.30	35.0
2.42	2.24	1.5:1	0.16	6	1.81	36.0
12.66	6.33	3:1	1.61	24	9.14	69.0

In the last experiment the quantity of nitrogen tetroxide used by the amine was slightly less than the quantity actually taken (12.66 g.) as the solvent, benzene, became completely saturated before the gas was wholly expelled from Bulb A. Hence this was taken as one limit in our experiments.

¹³ Meldola, *J. Chem. Soc.*, 47, 668 (1885).

Experiments with *p*-Nitro-aniline.—We succeeded in obtaining better yields of the diazonium nitrate with this amine than in the case of the *meta* compound. The identity of 4,4'-dinitrodiazo-amidobenzene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{N}:\text{N}\cdot\text{NHC}_6\text{H}_4\text{NO}_2$, was established by its correct melting point and comparison with a sample of the pure compound prepared according to the method of Meldola and Streatfeild.¹⁴ The compound can be crystallized from either alcohol or acetone and separates in canary-yellow prisms melting with decomposition from 225° to 230°, depending on the rate of heating. For quantitative determination of the *p*-nitrodiazonium nitrate formed this salt was coupled with β -naphthol in alkaline solution and weighed in the form of its azo dye, *p*-nitro-aniline red. This crystallized from toluene and was identical with the azo compound prepared for comparison by the well-known method of Meldola.¹⁵ The results of the five experiments with this amine are recorded in Table II.

TABLE II
DIAZOTIZATION OF *p*-NITRO-ANILINE WITH NITROGEN TETROXIDE

N_2O_4 , g.	<i>p</i> -Nitro-aniline, g.	Ratio of N_2O_4 to base	Diazo-amino compound		Azo dye, g.	Yield of diazonium nitrate, %
			G.	%		
2.52	7.56	1:2	6.6	84	1.3	12.0
2.40	3.60	1:1	1.24	34	2.44	32.0
4.34	4.34	1.5:1	0.38	9	4.84	53.0
7.86	5.92	2:1	0	..	7.71	61.0
5.55	3.72	2.25:1	0	..	7.13	91.0

It is to be noted that in the last two experiments no values for 4,4'-dinitrodiazo-amidobenzene are recorded. In each of these cases the precipitate first formed changed in consistency from a yellow flocculent condition to that of a gum and, finally, as the excess of nitrogen tetroxide was increased, was transformed into a heavy, amber-colored oil immiscible with benzene. On treating a drop of this oil with ether it changed immediately to the colorless *p*-diazonium nitrate which dissolved immediately in water. This salt was found to be very explosive.

Experiments with *o*-Nitro-aniline.—In this case the precipitate, which separated from the benzene solution of the amine, when treated with nitrogen tetroxide was almost black. As the gas continued to be passed into the solution the amount of precipitate finally ceased to increase, and then began to decrease as more nitrogen tetroxide was introduced. During this process the flaky precipitate changed gradually into a gum, and when the oxide was added in excess the gum finally underwent a complete transformation into a heavy, brown oil. This oil was changed immediately to a solid by trituration with a small volume of ether, and was identified as the *o*-diazonium nitrate. It coupled with β -naphthol to form the bril-

¹⁴ Meldola and Streatfeild, *J. Chem. Soc.*, 49, 624 (1886).

¹⁵ Ref. 13, p. 662.

liant red dye *o*-nitrobenzene-azo- β -naphthol, m. p. 209–210°, which has previously been described by Meldola and Hughes.¹⁶

The black precipitate, which separated in the first stage of the reaction, was found to be quite insoluble in water, but crystallized from boiling alcohol in yellow needles, m. p. 196°, corresponding in every way in its properties with 2,2'-dinitrodiazo-aminobenzene, which was prepared for comparison by the method of Meldola and Streatfeild.¹⁷ Of the three isomeric amines this *ortho* modification interacted far less smoothly with nitrogen tetroxide than its two isomers. The results obtained in five experiments are recorded in Table III.

TABLE III
DIAZOTIZATION OF *o*-NITRO-ANILINE WITH NITROGEN TETROXIDE

N_2O_4 , g.	<i>o</i> -Nitro-aniline, g.	Ratio of N_2O_4 to base	Diazo-amino compound		Azo dye, g.	Yield of diazonium nitrate, %
			G.	%		
3.12	9.36	1:2	1.17	12	1.62	8.0
3.17	4.66	1:1	0.98	10	0.20	4.0
6.49	6.49	1.5:1		0	3.54	28.0
5.36	4.02	2:1		0	2.33	27.0
9.02	6.00	2.25:1		0	6.35	64.0

Summary

1. It is shown that nitrogen tetroxide interacts with primary aromatic amines in anhydrous benzene to form the corresponding diazonium nitrate and diazo-amidobenzene combinations.
2. This reaction has thus far been applied successfully with aniline and *o*, *m* and *p*-nitro-anilines.
3. The mechanism of these changes are satisfactorily explained by assigning to nitrogen tetroxide the structure of nitrosyl nitrate, ON.O.NO₂.
4. Further evidence in support of the nitrosyl nitrate structure to express the chemical behavior of nitrogen tetroxide is presented.

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¹⁶ Meldola and Hughes, *J. Chem. Soc.*, 59, 374 (1891).

¹⁷ Meldola and Streatfeild, *ibid.*, 67, 52 (1899).