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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.]

THE USE OF NITROGEN TETROXIDE IN PLACE OF NITRIC ACID IN ORGANIC NITRATIONS¹

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It has been previously observed that when nitrogen tetroxide is allowed to react with organic substances, oxidation, nitration or diazotization may take place. In general, the experience of previous workers has been that both oxidation and nitration take place when a solution of nitrogen tetroxide in an organic substance is allowed to stand either in the dark or in sunlight for several weeks to several months. With nitro arylamines,² nitrogen tetroxide acts as a diazotizing reagent. It has also been found that solutions of nitrogen tetroxide in toluene and benzene form explosive mixtures.³

The reactions of oxides of nitrogen with organic substances described in the literature, as well as some preliminary experiments conducted in the course of this investigation, indicate that the direct nitration of organic substances with oxides of nitrogen is neither safe nor economically feasible, the chief objections being: (1) slowness of nitration at moderate temperature, (2) oxidation and (3) possible explosions at higher temperatures.

The present paper describes a study of the conditions governing the nitration of a number of aromatic compounds with nitrogen tetroxide in the presence of sulfuric acid.

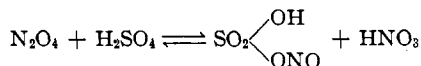
Theoretical

The fact that nitric acid oxidizes and only partially nitrates an organic substance, whereas a mixture of nitric and sulfuric acids yields a complete nitration, led to the belief that oxidation and explosion hazard might be avoided by using sulfuric acid in conjunction with the oxides of nitrogen. Sulfuric acid mixed with nitrogen tetroxide serves a purpose quite distinct from its use in the mixed acid nitration, for not only does it function as a dehydrating reagent, but it has the additional function of forming nitric acid *in situ* as shown in the following equation

¹ Presented before the Division of Organic Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Virginia, April 11-16, 1927.

² Houston and Johnson, *THIS JOURNAL*, **47**, 3011 (1925).

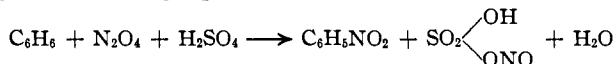
³ Raschig, *Z. angew. Chem.*, **35**, 117 (1922).



This equilibrium can be shifted practically completely to the right, for, according to the law of mass action $\frac{(\text{N}_2\text{O}_4)(\text{H}_2\text{SO}_4)}{(\text{HSO}_5\text{N})(\text{HNO}_3)} = K$, there are two factors involved in reducing the concentration of nitrogen tetroxide to a minimum, namely, the use of an excess of sulfuric acid and the constant removal of the nitric acid owing to its interaction with the organic substance, yielding a nitro compound.

The nitrosylsulfuric acid formed in the reaction and any unreacted sulfuric acid present in the mixture act as dehydrating reagents, thus facilitating the nitration of the organic substance.

In such a system, about 50% of the oxide of nitrogen is utilized in the nitration of the organic substance, and approximately 50% is combined with the sulfuric acid in the form of nitrosylsulfuric acid. The complete reaction for a single-step nitration for benzene, for example, can be represented by the following equation



The subsequent reaction of nitrosylsulfuric acid and water which one would expect is negligible, owing to the formation of a very stable solution of nitrosylsulfuric acid in concentrated sulfuric acid which stands dilution with water to some extent with the establishment of corresponding equilibria.

Nitration of Benzene

Work, therefore, was undertaken to determine the practicability of this method as applied to the nitration of benzene. The apparatus used in these experiments consisted of a wide-mouthed bottle with a ground-glass joint bearing a mercury seal for a stirrer. Just below the neck of the bottle were sealed to it a dropping funnel and a capillary tube with a stopcock. In general, the method of procedure was as follows. To a solution in the bottle consisting of 1.05 moles of nitrogen tetroxide in 1.25 to 1.75 moles of sulfuric acid, having a concentration ranging between 85 and 95%, a mole of benzene was slowly added from the dropping funnel. During the addition the temperature of the reaction mixture was maintained at 5 to 15°, and subsequent to the mixing of the reactants the temperature was raised to 40–60°, the working temperature range being essentially that recommended in the ordinary nitration of benzene. The reaction mixture was agitated during the addition and afterwards until the reaction was complete, the total time for each run being five hours. The stopcock on the capillary tube was turned whenever there was an appreciable difference between the internal and external levels of the mercury in the seal of the stirrer.

The yields found were somewhat lower than the true yields, owing to the small losses in the various steps in the process. The quantity of material used in each of these experiments was relatively small (25 cc. of benzene), hence the sum total of the various losses was a fair percentage of the total, and it was believed that a few of the actual yields were similar to those obtained in commercial practice.

The data of the more significant experiments are recorded in the following table.

TABLE I
NITRATION OF BENZENE
Molecular ratio of N_2O_4 to C_6H_6 = 1.05

Expt. No.	Moles $H_2SO_4^a$	Concn. of H_2SO_4	Temp., °C.	Yield of nitrobenzene (steam distilled), %
1	1.25	95	40-50	81.3
2	1.50	95	50-60	89.5
3	1.75	95	55-60	94.4
4	1.25	85	40	70.2
5	1.50	85	40-50	80.7
6	1.50	90	40-50	86.3

^a Per mole of benzene.

An examination of the table shows that there are the following possible variables, namely, (1) ratio of nitrogen tetroxide to benzene, (2) ratio of sulfuric acid to benzene, (3) concentration of the sulfuric acid and (4) temperature.

With regard to the ratio of nitrogen tetroxide to benzene, it has been previously stated that theoretically they should be molecular. However, in practice a slight excess of the oxide of nitrogen is preferable, for the purpose of hastening the final stage of the nitration as well as taking care of any volatilization of the nitrogen tetroxide. Hence, a molecular ratio of 1.05 nitrogen tetroxide was selected and was found to be very satisfactory.

As shown by the experimental data, it is more desirable to use a large excess of sulfuric acid. By using a higher molecular ratio of sulfuric acid, for example, 1.75, the nitration can be carried out at higher temperatures (55-60°) without any appreciable loss of the oxide of nitrogen, and consequently the reaction is completed in a shorter period of time.

The concentration of the sulfuric acid is a very important factor which is dependent upon the nature of the substance to be nitrated and upon the quantity of sulfuric acid used. It is well known that in the nitration of substances which are readily nitrated lower acid concentrations are more desirable than "concentrated" or fuming sulfuric acid. By maintaining the molecular ratio of sulfuric acid to benzene constant, a variation in the concentration of the sulfuric acid from 85 to 95% effects a 9-11% increase in yield of nitrobenzene. However, the higher yields can be obtained by using greater quantities of sulfuric acid of the lower concentration.

The temperature is determined by the quantity and concentration of the sulfuric acid.

Nitration of Mononitrobenzene

When 2 moles of nitrogen tetroxide and from 2.5 to 3 moles of concentrated and fuming sulfuric acid per mole of benzene were used, several unsuccessful attempts to effect a two-step nitration were made.

However, a 93.4% yield of dinitrobenzene was obtained by slowly adding a mole of nitrobenzene to a solution of 1.05 moles of nitrogen tetroxide in 2.8 moles of fuming sulfuric acid (containing 4.28 parts of free SO_3).

The effect owing to the variation of the molecular ratio and concentration of the sulfuric acid is shown in the following table.

TABLE II
NITRATION OF NITROBENZENE

Expt. No.	Moles of N_2O_4	Moles of H_2SO_4^a	Concn. of H_2SO_4	Time (hrs.)	Temp., $^{\circ}\text{C}$.	Yield of di-nitrobenzene
1	1.1	2.8	104.3	$1\frac{1}{2}$	60-75	93.4%
2	1.05	2.0	104.3	$1\frac{1}{2}$	60-75	86.4
3	1.05	1.75	104.3	3	60-75	69.6
4	1.05	1.5	104.3	$2\frac{1}{2}$	60-70	49.3
5	1.1	2.7	95	$2\frac{1}{4}$	60-70	84.3
6	1.05	2.5	95	$2\frac{1}{4}$	55-70	55.0
7	1.05	2.0	95	$2\frac{1}{2}$	60-75	40.7
8	1.05	1.5	95	3	55-70	17.5

^a Per mole of nitrobenzene.

Nitration of Toluene

Nitrotoluene was synthesized by adding a mole of toluene to a solution of 1.05 moles of nitrogen tetroxide in 1.6 moles of 95% sulfuric acid. The reaction mixture was agitated for three and one-half hours at a temperature of 50-55°, and at the end of the reaction the excess toluene was removed by vacuum distillation. The yield of nitrotoluene was 87.5% of the theoretical.

Nitration of Naphthalene

α -Nitronaphthalene was obtained by the reaction of 1.0 moles of naphthalene with a solution of 1.1 moles of nitrogen tetroxide and 1.5 moles of 95% sulfuric acid. The experimental procedure was similar to that used in the nitration of naphthalene with mixed acid. The yield of purified α -nitronaphthalene, recrystallized from alcohol, was 88.4% of the theoretical.

Summary

1. A method for the nitration of organic substances with nitrogen tetroxide in the presence of sulfuric acid is described, benzene, nitrobenzene, toluene and naphthalene being used as examples.

2. The method involves an intermediate reaction of the nitrogen tetroxide with the sulfuric acid whereby nitrating and dehydrating reagents are simultaneously formed.

3. The yields of the nitro compounds range from 87% to upwards of 90% of the theoretical.

WASHINGTON, D. C.