the formation of the lake, but the addition of ammonium hydroxide to a solution containing aluminum and phosphate ions gives a precipitate with a ratio of phosphate to aluminum low enough to make the test satisfactory.

A quantity of aluminum equal to 2 × 10^{-5} mole gives immediate precipitation; smaller amounts show precipitation or a red solution easily distinguishable from the yellow of the dye in alkaline solution. The delicacy of the test is of the order of 10^{-6} mole of aluminum.

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NITRATION BY MEANS OF A MIXTURE OF NITROSULFONIC AND FUMING NITRIC ACIDS

BY PHULDEO SAHAY VARMA AND DATTATREY ANANT KULKARNI

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A survey of the literature shows the lack of any systematic study of the nitrating action of nitrosulfonic acid. Also the mechanism of its nitrating action is not clear, whether it is direct nitration or whether the nitrosulfonic acid first acts as a dehydrating agent, decomposing into products which then bring about nitration or nitrosation. Moreover, its constitution has not yet been definitely established[1] whether it be $HO.SO_2.ONO$, nitrosylsulfuric acid, or $HO.SO_2.NO_2$, nitrosulfonic acid. Its action on dimethylaniline depends on the temperature, high temperature favoring nitration and low temperature nitrosation.

Girard and Pabst[2] obtained the nitroso derivatives of fluorescein and alizarin by the action of nitrosylsulfuric acid in sulfuric acid solution; from aniline and naphthalene in the presence of acetic acid and hydrochloric acid, respectively, the products were amino-azobenzene and chrysoidine and aniline sulfate. Deninger[3] obtained 3-nitro-4-hydroxybenzoic acid from *p*-hydroxybenzoic acid, and Markownikoff[4] found that nitrosulfonic acid is a stronger nitrating agent for saturated aliphatic hydrocarbons than nitric acid itself. From *p*-hydroxybenzoic acid Biehringer and Borsum[5] obtained besides 3-nitro-4-hydroxybenzoic acid also small amounts of 2,4-dinitrophenol and 3-sulfonic-4-hydroxybenzoic acid

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[1] Biehringer and Borsum, *Ber.*, **49,** 1402 (1916).

[2] Girard and Pabst, *Bull. soc. chim.*, **30,** 532 (1878); *Ber.*, **12,** 365 (1879).

[3] Deninger, *J. prakt. Chem.*, [2] **42,** 552 (1890).

[4] Markownikoff, *Ber.*, **32,** 1441 (1899); **35,** 1584 (1902).

[5] Biehringer and Borsum, *Ber.*, **48,** 1314 (1915).

and from dimethylaniline[1] both *p*-nitro- and *p*-nitroso-dimethylaniline. Heinemann[6] proposes nitrosylsulfuric acid for the absorption of the water formed during the nitration of hydrocarbons but he gives no experimental details. Recent study of absorption spectra[7] of sulfuric acid solutions of nitrosylsulfuric acid leads to the conclusion that it is present as nitrosulfonic acid and that it is not decomposed in aqueous sulfuric solution as dilute as 20%.

The object of this work was threefold: to determine (1) whether any light is thrown upon the question of the structure of nitrosylsulfuric acid by its nitrating action on aromatic compounds; (2) whether it acts as a dehydrating or as a nitrating agent; (3) whether it can conveniently and economically be employed as a nitrating agent.

Experimental Part

The nitrosulfonic acid was prepared by passing a stream of sulfur dioxide into cold fuming nitric acid (d., 1.502) until about a 50% yield was obtained. Most of the nitrations were carried out at room temperature, about 30°. The reaction is generally very vigorous and must be moderated by cooling the reaction flask. In a few cases the action was so vigorous as to cause complete charring. The yield in several cases was quantitative, and as a rule the products were free from by-products. The amount of nitrosulfonic-nitric acid mixture necessary is considerably less than that of the sulfuric-nitric acid mixture usually employed. A summary of the nitration experiments is given in Table I.

Crystals of nitrosylsulfuric acid have no effect on benzene, whereas a mixture of benzene, sulfuric and nitrosylsulfuric acids blackens when warmed and emits the odor of burnt sugar but yields no nitrobenzene. However, when a 46% solution of nitrosulfonic acid in fuming nitric acid was used, a good yield of nitrobenzene was obtained. The mixture of nitrating acid and benzene was shaken for a few minutes, heated on a water-bath for 0.5 hour, and then poured into water. The nitrobenzene was separated, dried over calcium chloride and distilled. The effect of the amount of nitrating mixture is shown by the following results. Using 5 g. of benzene the yield of nitrobenzene increased from 1.5 g. with 7 g. of nitrating mixture to a maximum of 5.1 g. with 18.5 to 22.0 g. of nitrating mixture and then decreased to 3.5 g. with 45 g. of nitrating mixture.

When the amount of acid mixture is too large or the time of heating longer than 0.5 hour, some dinitrobenzene is produced. However, conversion to the dinitro derivative is not complete even when double the optimum amount of acid mixture is used and the heating prolonged for five hours; about 20% of the benzene appears as dinitro- and the rest as

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[6] Heinemann, Brit. pat. 102,216.

[7] Schlesinger and Salathe, THIS JOURNAL, **45**, 1863 (1923).

TABLE I

NITRATION EXPERIMENTS

Starting material	Product
5 g. of benzene + 18.5 g. of nitrating mixture	5.1 g. of nitrobenzene (b. p., 209–210°)
25 g. of toluene	12 g. of *o*- (b. p., 219–223°) + 10 g. of *o*-, and *m*- (b. p., 225–228°) + 5 g. of *p*-nitrotoluene (b. p., 229–231°)
5 g. of *m*-xylene + 18 g. of nitrating mixture	3.5 g. of 4-nitro-*m*-xylene (b. p., 235–238°)
5 g. of mesitylene + 18 g. of nitrating mixture	3 g. of nitromesitylene
5 g. of naphthalene + 7.5 g. of nitrating mixture	α-nitronaphthalene (m. p., 54°; quantitative yield)
anthracene	charring + small amount of anthraquinone
10 g. of chlorobenzene + 12.5 g. of nitrating mixture	8 g. of *p*-nitro-chlorobenzene (b. p., 81–82°)
bromobenzene	*p*-nitro-bromobenzene (m. p., 126°; quantitative yield)
iodobenzene	*p*-nitro-iodobenzene (m. p., 175°; quantitative yield)
phenol	charring
7 g. of *o*-nitrophenol + 12 g. of nitrating mixture	2,5-dinitrophenol (m. p., 103–104°)
9 g. of *o*-nitrophenol + 36 g. of nitrating mixture	8 g. of a mixture of 2,5-dinitrophenol, 2,4,5-trinitrophenol (m. p., 94–96°) + unidentified products
aniline	charring
o-nitro-aniline	charring
5 g. of *p*-nitro-aniline + 15 g. of nitrating mixture + 10 g. of acetone	2,4-dinitro-aniline + 2,4,6-trinitro-aniline (m. p., 186–188°)
5 g. of benzaldehyde + 7 g. of nitrating mixture	benzoic acid (m. p., 120°)
5 g. of benzoic acid + 20 g. of nitrating mixture	4.5 g. of *m*-nitrobenzoic acid (m. p., 138°)
5 g. of salicylic acid + 20 g. of nitrating mixture	5-nitrosalicylic acid (m. p., 224–225°; $COOH:OH:NO_2 = 1:2:5$)
5 g. of *m*-cresotinic acid ($COOH:OH:CH_3 = 1:2:4$) + 10 g. of nitrating mixture	6-nitro-*m*-cresotinic acid (m. p., 216–217°; $COOH:OH:CH_3:NO_2 = 1:2:4:6$; good yield)
5 g. of *p*-cresotinic acid + 7 g. of nitrating mixture + 10 g. of acetone	3-nitro-*p*-cresotinic acid (m. p., 82°; not pure)
5 g. of *o*-cresotinic acid ($COOH:OH:CH_3 = 1:2:3$) + 10 g. of nitrating mixture + 10 g. of acetone	1 g. of 5-nitro-*o*-cresotinic acid (m. p., 195–198°)
5 g. of benzanilide + 18 g. of nitrating mixture + 10 g. of acetone	nitrobenzanilide (m. p., 156°)

mononitrobenzene. A trace of iodine catalytically favors the formation of the dinitro derivative.[8]

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[8] This aspect of the problem will be the subject of a subsequent communication.

With *m*-xylene and mesitylene considerable residue remained in the distilling flask. Here, as in ordinary nitration, the reaction becomes more vigorous with increase in the number of methyl groups.

Phenol treated directly or in the presence of diluents is instantly charred but the nitrophenols give good yields. The nitration product of *o*-nitrophenol after crystallization from alcohol melted at 103–104° and was identified as 2,5-dinitrophenol.

Anal. Subs., 0.137: N, 19.8 cc. (28°, 756.5 mm.). Calcd. for $C_8H_4O_5N_2$: N, 15.2. Found: 16.0.

When a larger amount of nitrating mixture was used the product was a mixture of 2,5-di- and 2,4,5-trinitrophenols. Nine g. of *o*-nitrophenol in 36 g. of nitrating mixture was warmed on a water-bath for 0.5 hour and then poured into water. The yellow solid thus obtained was fractionally crystallized from alcohol.

TABLE II

NITRATION OF PHENOL

Fraction	M. p. °C.	Product	Yield G.
I	102–103	2,5-dinitrophenol	2.5
II	96–98	mixture	2.0
III	94–96	2,4,5-trinitrophenol	1.0
IV	85–86	not yet identified	1.5
V	78–82	not yet identified	1.0

Anal. FRACTION I. Subs., 0.098: N, 14.3 cc. (27°, 756 mm.). Calcd. for $C_6H_4N_2O_5$: N, 15.2. Found: 16.2. (Some of the trinitro derivative was probably present.)

FRACTION III. Subs., 0.126: N, 21.4 cc. (28°, 756 mm.). Calcd. for $C_6H_3O_7N_3$: N, 18.3. Found: 18.8.

Aniline, mono- or dimethylaniline, treated directly or after dilution with acetone or chloroform was quickly charred. As the nitrating acid was slowly added, each drop produced a slight explosion. The reaction was also tried at lower temperatures but as soon as the flask was removed from the ice-bath and the temperature allowed to rise, charring again took place. The nitro-anilines react less energetically but the products from *o*- and *m*-nitro-anilines are complex and have not yet been completely separated and identified.

Benzoic acid is nitrated very smoothly. To 5 g. of benzoic acid was added 20 g. of the nitrating acid, the mixture was warmed a few minutes and then poured into cold water. The white solid was washed with water and crystallized from alcohol. It melted at 138° and was identified as *m*-nitrobenzoic acid; yield, 4.5 g. The low melting point was due to the presence of a trace of benzoic acid.

In the case of *o*- and *p*-cresotinic acids, charring may be avoided by the use of acetone as diluent and slow addition of the nitrating acid to the cold acetone solution. In both cases digestion with warm water removes a portion of the reaction product consisting partly of unchanged starting material and partly of unidentified products.

Summary

1. A 45–50% solution of nitrosulfonic acid in fuming nitric acid, prepared by passing sulfur dioxide into cold fuming nitric acid, is a better nitrating agent than the usual mixture of nitric and sulfuric acids.

2. This reagent has been employed to nitrate various phenols, anilines, aromatic acids and hydrocarbons, as well as benzanilide and benzaldehyde.

3. It is suggested that nitrosulfonic acid functions because of its dehydrating action. In this respect it is more efficacious than sulfuric acid; hence the amount of nitrosulfonic acid necessary is considerably less than that of sulfuric acid ordinarily employed in nitrating mixtures.

BENARES, INDIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

SYNTHESIS OF THE POLYPEPTIDE-HYDANTOIN: N-1-METHYL-TYROSYL-HYDANTOIN-3-ACETIC ACID

BY DOROTHY A. HAHN AND ALICE G. RENFREW[1]

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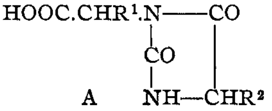
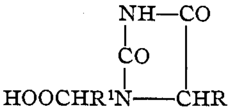
The combination of α-amino acids in such a manner as to produce cyclic urea combinations has been discussed in an earlier paper by Treat B. Johnson.[2] Such substances on hydrolysis yield α-amino acids and carbon dioxide as the sole products of decomposition and, since they may be regarded as representatives of a new class of hydantoins, have been given the name of *polypeptide-hydantoins*. Compounds of this type in all cases contain an acid group in place of a hydrogen atom in the N-1 position of the hydantoin ring as indicated by the general formula, A



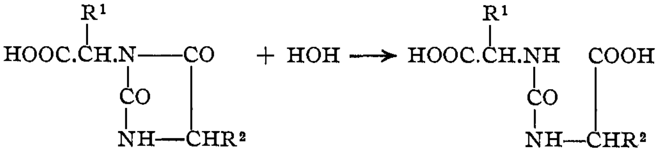
A



B

When subjected to intense hydrolysis such substances undergo a decomposition of the hydantoin ring which may be regarded as taking place in two stages according to the following mechanism,

(a)



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[1] The work which is embodied in this paper is being offered in partial fulfilment of the requirements for the degree of Master of Arts at Mount Holyoke College.

[2] Johnson, *Proc. Nat. Acad. Sci.*, **2**, 69 (1916).