[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE OXYNITRATION OF BENZENE TO 2,4-DINITROPHENOL[1]

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During World War II there was interest for a time in the preparation of picric acid by oxynitration of benzene. In this process, discovered by Wolffenstein and Boeters (1), benzene is converted into picric acid by the action of a hot solution of mercuric nitrate in nitric acid. The history and mechanism of the oxynitration reaction have been discussed in recent papers (2, 3).

Downing, Robertson, and Wright (4) developed a procedure for obtaining picric acid from benzene in one operation. The addition of benzene to a solution of mercuric nitrate in 50% nitric acid containing small amounts of aluminum and manganese ions at 65° was followed by a "boil-up" of the mixture at 115–120°. In the present study it was planned to work out conditions whereby 2,4-dinitrophenol could be prepared by oxynitration of benzene and then nitrated to picric acid by a nitrating agent more effective than the oxynitration mixture. A few runs indicated that the conversion of 2,4-dinitrophenol into picric acid by means of the oxynitration mixture was about 82% in contrast to the 96% conversion that could be effected with mixed acid. Wolffenstein and Boeters (1) had obtained 2,4-dinitrophenol by various procedures.

After considerable experimentation 72% yields of 2,4-dinitrophenol containing a few per cent of picric acid could be obtained based on the benzene that entered into the reaction. Benzene was added dropwise to a stirred solution of 10.65 molar nitric acid which was 0.37 molar with respect to mercuric nitrate; the temperature was kept constant at 50°. In Table I are shown the products obtained when the optimum conditions were employed; the yields are based on the benzene actually consumed and not on the amount added (about 7.5% of benzene escapes in the evolved gases).

It is seen that the by-products included nitrobenzene, *o*- and *p*-dinitrobenzene, and 2,4,2′,4′-tetranitrodiphenylamine, in addition to carbon dioxide and oxalic acid. The presence of 2,4,2′,4′-tetranitrodiphenylamine in the oxynitration mixture had not been reported previously.

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[1] This investigation was carried out under contract OEMsr-245, recommended by the National Defense Research Committee, between the Regents of the University of Michigan and the Office of Scientific Research and Development in close collaboration with three other groups: Carmack, Baizer, Handrick, Kissinger, and Specht of the University of Pennsylvania; Westheimer, Segel, and Schramm of the University of Chicago; and Wright of the University of Toronto. The earlier work of the latter served as a useful guide in the investigation.

We are happy to acknowledge the aid of Dr. Ralph Connor who was Chief of the section in which this work was done and who suggested to us that 2,4-dinitrophenol rather than picric acid be prepared in the oxynitration reaction.

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The effect of temperature, rate of benzene addition, and concentration of reagents on the yield and on the rate of 2,4-dinitrophenol formation were studied. The effect on the yield was determined by a batch procedure while the effect on the rate of the reaction was studied more conveniently by a continuous process.[3]

A temperature of 50° was found to be the optimum temperature for preparing 2,4-dinitrophenol by the oxynitration reaction by our procedure. At higher temperatures more of the 2,4-dinitrophenol was nitrated to picric acid with consequent lowering in yield, and more nitrobenzene was produced; thus, at 70° the combined yield of 2,4-dinitrophenol (16.9%) and picric acid (37.7%) was only 54.6% and the yield of nitrobenzene was 17–19%. At 40° the reaction was slower and the yield of 2,4-dinitrophenol was not increased.

The rate of addition of benzene is an important factor in determining the ratio of 2,4-dinitrophenol to nitrobenzene. If the benzene was added at such a rate that a liquid benzene phase was present in the stirred oxynitration mixture, considerable nitration of the benzene took place at the expense of the oxynitration reaction. Thus, when all the benzene was added at the start of the experiment, the combined yield of 2,4-dinitrophenol and picric acid was 48.5% and the yield of nitrobenzene was 24.7%. As the addition time was increased, the yield of 2,4-dinitrophenol increased and that of nitrobenzene decreased until an optimum time was reached for the amounts and products recorded in Table I. However, no matter how long a time was taken for the addition of the benzene, a certain irreducible minimum of nitrobenzene was formed. This result suggested that some of the nitrobenzene is formed from an intermediate in the oxynitration reaction, probably nitrosobenzene, as suggested by Desvergnes (5).

TABLE I

PRODUCTS OBTAINED BY OXYNITRATION OF BENZENE AT 50°

COMPOUND	YIELD, %
2,4-Dinitrophenol	68.4
Picric acid	4.0
Nitrobenzene	7.8
o-Dinitrobenzene	0.07
p-Dinitrobenzene	1.0
2,4,2′,4′-Tetranitrodiphenylamine	0.05
Carbon dioxide	9.7
Oxalic acid	2.5

Increasing the mercuric ion concentration markedly increased the rate of reaction (6), but had little effect on the yield of 2,4-dinitrophenol. Although aluminum ion has been employed by others in the oxynitration reaction, no beneficial effect was observed in the preparation of 2,4-dinitrophenol under the conditions of the present investigation. Although an increase in the concentra-

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[3] The details of these studies are too extensive to be included here. The descriptions of the procedures and the diagrams of the apparatus appear in OSRD report 4026.

tion of nitric acid markedly increased the rate of the reaction, it also favored the formation of nitrobenzene.

The chief function of manganese ion in the oxynitration reaction when it is employed is to catalyze the oxidation of the by-product oxalic acid by the nitric acid. This is of importance when the oxynitration solution is used repeatedly. If the oxalic acid is not destroyed, eventually a concentration is reached when solid mercuric oxalate precipitates; in the presence of sufficient manganous ion the concentration of the oxalic acid can be kept below the precipitation point and the oxynitration mixture can be used repeatedly provided the nitric acid concentration is maintained (conveniently by the addition of 98% nitric acid). The manganous ion also increases somewhat the rate of oxynitration and catalyzes the nitration of 2,4-dinitrophenol to picric acid.

It has been proposed (2, 3) that nitrosobenzene, benzenediazonium nitrate, and phenol are intermediates in the oxynitration reaction. In order to test this point we studied the behavior of these compounds in the oxynitration mixture under the same conditions employed for the oxynitration of benzene. The results are shown in Table II.

TABLE II

ACTION OF OXYNITRATION MIXTURE ON THREE INTERMEDIATES

COMPOUND	PRODUCTS;[a] YIELD, %			
	DNP	NB	DNB	Oxalic acid
Nitrosobenzene	67.9	6.6	1.3[b]	3
Benzenediazonium nitrate	69.5	0	0	5
Phenol	71.3	0	0	6

[a] Abbreviations: DNP = 2,4-dinitrophenol; NB = nitrobenzene; DNB = crude dinitrobenzene.

[b] The major portion of this fraction was 2,4,2′,4′-tetranitrodiphenylamine.

In each of the three experiments the yield of 2,4-dinitrophenol[4] (which was of high quality and contained only a little picric acid) was in the neighborhood of 70% and approached the yield obtained by oxynitration of benzene. The formation of nitrobenzene in 6.6% yield by oxynitration of nitrosobenzene is additional evidence that not all of the nitrobenzene formed in the oxynitration of benzene arises from direct nitration of benzene.

EXPERIMENTAL

Preparation of 2,4-dinitrophenol from benzene. A 1.5-liter three-necked flask was fitted with an Ace Trubore stirrer with a half-moon paddle. One neck was fitted with a condenser and the other with a long-stemmed dropping-funnel which dipped below the surface of the solution. Ground-glass connections were used throughout.

In the flask was placed 750 cc. of a solution 10.65 molar in nitric acid and 0.37 molar in mercuric nitrate prepared by adding 60 g. of mercuric oxide to 541 cc. of 70% nitric acid and

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[4] Carmack and co-workers obtained 2,4-dinitrophenol by the action of 50% nitric acid on benzenediazonium nitrate and on phenol and by the action of nitric oxide followed by nitric acid on nitrosobenzene.

diluting with water to 750 cc. About 0.1 g. of sodium nitrite was added to eliminate any induction period. To the stirred solution held at 50°, 50 g. of thiophene-free benzene was added at a continuous rate in the course of three and one-third hours. The mixture was stirred for an additional two and two-thirds hours at 50° and then chilled for twelve hours. The pale-tan colored precipitate of 2,4-dinitrophenol (containing less than 0.1% of picric acid) was filtered on a sintered-glass funnel and washed with two 50-cc. portions of 50% nitric acid and three 50-cc. portions of cold water; yield, 67 g.; m.p. 112–113°.

The filtrate and washings were extracted with three 100-cc. portions of benzene, and the combined benzene extracts were shaken with 30% aqueous triethanolamine (suggested by G. F Wright). Acidification of the basic solution with concentrated hydrochloric acid precipitated a mixture of 7.5 g. of 2,4-dinitrophenol and 5.5 g. of picric acid. The total yields of all products are shown in Table I. The same results were obtained when the benzene was added in five 10-g. portions at sixty-minute intervals.

When the oxynitration liquor was used repeatedly, the nitric acid concentration was maintained by adding 18 cc. of 98% nitric acid after each 10 g. of benzene. The benzene (about 7.5%) that escaped with the evolved gases was determined by passing the gases through a Drechsel bottle containing 60 cc. of 98% nitric acid and 75 cc. of 95% sulfuric acid. The *m*-dinitrobenzene which was obtained by drowning the mixture in 750 cc. of ice and water and extracting with benzene was weighed.

Estimation of by-products. The oxalic acid which was formed was determined by adding calcium chloride to an aliquot of the oxynitration liquor, followed by addition of dilute aqueous ammonia. The calcium oxalate which precipitated was isolated and titrated in dilute sulfuric acid with standard potassium permanganate.

The carbon dioxide was determined by washing the evolved gases with ferrous sulfate solution, drying with calcium chloride and then absorbing the carbon dioxide in 40% potassium hydroxide solution.

The benzene solution remaining after the triethanolamine extraction was distilled. The fraction boiling at 190–210° was collected as nitrobenzene. Somewhat over 11 g. of the residues from several runs was steam distilled in order to remove nitrobenzene (5.51 g.), and the residual solid was subjected to fractional crystallization from benzene, chloroform, and ethanol with the aid of mechanical separation. In this manner there were obtained 0.37 g. of *o*-dinitrobenzene (0.26 g. with m.p. 116–117°), 5.02 g. of *p*-dinitrobenzene (4.58 g. with m.p. 171.5–174°) and 0.24 g. of 2,4,2′,4′-tetranitrodiphenylamine (m.p. 201–203°).

The 2,4,2′,4′-tetranitrodiphenylamine was identified by color tests (7), by its weakly acidic character (several extractions with 5% sodium hydroxide did not remove it completely from a benzene solution), by a mixed m.p. with an authentic specimen, by conversion of a sample to dipicrylamine, and by analysis.

Anal. Calc'd for $C_{12}H_7N_5O_8$: C, 41.3; H, 2.0; N, 20.1.
Found: C, 42.1; H, 2.4; N, 19.7.

Determination of picric acid. The method was based on the selective precipitation of nitron picrate from an aqueous acidic medium. Three grams of nitron reagent was dissolved in 25 cc. of 5% aqueous acetic acid and the filtered solution (after decolorization with Norit) was used immediately.

One-tenth gram of a 2,4-dinitrophenol-picric acid mixture was dissolved in 125 cc. of boiling water containing 2 cc. of aqueous sulfuric acid (prepared from 2 volumes of concentrated acid and 3 volumes of water), 5 cc. of the nitron solution was added, and the mixture was allowed to cool to room temperature in cold water for exactly one hour; if a longer time is allowed precipitation of brown nitron dinitrophenolate may occur. The yellow flocculent precipitate of nitron picrate was filtered on a weighed sintered-glass crucible, washed with 10–20 cc. of water, and dried at 75° for at least an hour. The weight of the precipitate multiplied by 0.4231 gave the weight of picric acid.

The method was checked with samples of known composition and with samples of dinitrophenol-picric acid mixtures from the oxynitration reaction to which additional picric acid had been added. Picric acid up to 20% in the mixtures could be determined to within 0.5%.

Nitration of 2,4-dinitrophenol to picric acid. A solution of 10 g. of 2,4-dinitrophenol in

25 cc. of warm concentrated sulfuric acid was cooled to 25° (partial crystallization set in) and 2.5 cc. of 98% nitric acid was added dropwise to the swirled mixture. The mixture was kept at room temperature for fifteen minutes and then at 65° for the same length of time. Drowning with 250 cc. of water yielded 11.96 g. (96.5%) of picric acid; m.p. 121–122.5° with previous sintering.

Effects of manganous ion in the oxynitration mixture. Oxalic acid is not appreciably oxidized by nitric acid (10.6 to 13 *M*) at the temperatures (45–60°) at which the oxynitration is generally carried out. In a liter of 10.65 *M* nitric acid and 0.37 *M* mercuric nitrate solution at 50° to which oxalic acid was added, 16 g. of oxalic acid remained in solution at equilibrium (after no more solid mercuric oxalate precipitated). The equilibrium point is reached slowly so that a greater concentration of oxalic acid may be reached for a time, but eventually the mercuric oxalate precipitates. If the manganous ion concentration in the oxynitration mixture is 0.67 *M*, the oxalic acid concentration rises to about 11.5 g. per liter but no further, and no mercuric oxalate precipitates. With this concentration of manganous ion in the oxynitration mixture, the products and yields were: 54.2% 2,4-dinitrophenol, 13.9% picric acid and 9.2% nitrobenzene.

The catalytic effect of manganous ion on the nitration of 2,4-dinitrophenol to picric acid was shown by the following experiments. When a suspension of 10 g. of 2,4-dinitrophenol in 50 cc. of 10.65 *M* nitric acid was kept at 50° for twenty-four hours with occasional swirling, the yield of picric acid was less than 2%. When the same mixture was 0.42 *M* with respect to manganous ion, a 32% yield of picric acid was obtained under the same conditions. This result explains the larger percentage of picric acid in the oxynitration product (see preceding paragraph) when manganous ion is present.

Conversion of nitrosobenzene, benzenediazonium nitrate, and phenol to 2,4-dinitrophenol by the oxynitration mixture. In three separate experiments 0.642 mole quantities (corresponding to 50 g. of benzene) of these three compounds were added to 750 cc. of a stirred solution 10.65 *M* in nitric acid and 0.37 *M* in mercuric nitrate over a period of two and one-half hours, and the mixture was stirred for an additional half hour; the temperature was kept at 50° and the nitric acid concentration was maintained by continuous addition of 98% nitric acid. The benzenediazonium nitrate and the phenol were added in the form of concentrated aqueous solutions. The reaction mixtures were worked up in the manner described for the oxynitration of benzene. The products are recorded in Table II.

SUMMARY

The preparation of 2,4-dinitrophenol by the oxynitration of benzene by a solution of mercuric nitrate in nitric acid is described.

The effects of various factors on the rate of the reaction and on the yield of 2,4-dinitrophenol are discussed.

Nitrosobenzene is oxynitrated to 2,4-dinitrophenol.

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REFERENCES

(1) WOLFFENSTEIN AND BOETERS, *Chem. Abstr.*, **2,** 489, 1861 (1908); **4,** 369 (1910); *Ber.*, **46,** 586 (1913).
(2) WESTHEIMER, SEGEL, AND SCHRAMM, *J. Am. Chem. Soc.*, **69,** 773 (1947).
(3) CARMACK, BAIZER, HANDRICK, KISSINGER, AND SPECHT, *J. Am. Chem. Soc.*, **69,** 785 (1947).
(4) DOWNING, ROBERTSON, AND WRIGHT, *Ind. Eng. Chem.*, in press.
(5) DESVERGNES, *Chimie & Industrie*, **22,** 451 (1929).
(6) Compare DAVIS, WORRALL, DRAKE, HELMKAMP, AND YOUNG, *J. Am. Chem. Soc.*, **43,** 594 (1921).
(7) DAVIS AND ASHDOWN, *J. Am. Chem. Soc.*, **46,** 1051 (1924).