1.5187, $\alpha^{25}D$ +12.4° (neat, *l* 1 dm.). Comparison of the infrared spectrum of this alcohol with authentic samples of IX, X and XI indicated that neither the tertiary (IX) nor the primary (X) alcohols were present in detectable amounts.

When 0.4 g. of XI, $n^{25}D$ 1.5189, $\alpha^{25}D$ +9.10° (neat), was treated with 4.0 g. of W-1 Raney nickel (reflux in 20 ml. of absolute ethanol for 21 hours) there was obtained 0.32 g. of alcohol, $\alpha^{24}D$ +11.6° (neat, *l* 1 dm.), $n^{25}D$ 1.5186, no hydrocarbon being detected. The following explanation is offered to correlate the rotational changes observed. Lithium aluminum hydride reduction of (+)-VII would be expected to give rise to a diastereomeric mixture of 3-methyl-3-phenyl-2-pentanols in which the *erythro* isomer predominated.[17a] By analogy with the previous systems in this series of studies, the *erythro* isomer would be expected to have a lower optical rotation than the *threo* isomer (one exception to this generalization was recently encountered[17e]). Treatment with W-1 Raney nickel has afforded at least partial equilibration to a mixture of alcohols having a greater proportion of *threo* diastereomer and, consequently, a higher optical rotation.

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[CONTRIBUTION FROM THE ORGANIC CHEMISTRY BRANCH, CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

Reactions of Nitrate Esters. II. Reactions with Hydrazine[1,2]

BY RAYMOND T. MERROW AND ROBERT W. VAN DOLAH

RECEIVED FEBRUARY 27, 1954

It has been found that, with sufficiently high concentrations, simple nitrate esters react with hydrazine at ordinary temperatures in the absence of catalysts. Primary aliphatic nitrates undergo reduction and substitution, yielding nitrogen, nitrous oxide, ammonia, hydrazoic acid, nitrite ion, nitrate ion, alkylated hydrazines, alcohol and traces of aldehyde. High hydrazine concentrations favor the reduction process. A mechanism is proposed for the reduction, based on other known reactions of nitrate esters and on postulated mechanisms for other oxidations of hydrazine. Benzyl nitrate reacts primarily by the substitution process, although a small amount of reduction also occurs with high concentrations of hydrazine. Some α-hydrogen elimination apparently occurs, forming benzaldehyde and nitrous acid. *t*-Butyl nitrate undergoes β-elimination almost exclusively, giving isobutylene and nitrate ion. Small amounts of substitution products are also obtained, but no nitrogen or nitrogen oxides are formed.

Hydrazines have long been known as strong reducing agents toward most inorganic and some organic oxidizers, including nitro compounds and nitrite esters, but only a very limited amount of information has been published regarding their reactions with nitrate esters. The reaction of phenylhydrazine with ethyl nitrate at elevated temperatures, giving nitrogen, aniline and ammonium nitrate, was reported in 1896.[3] From the same reactants at ordinary temperatures in the presence of sodium ethoxide, Bamberger and Billeter[4] obtained nitrite ion, nitrogen, benzene, biphenyl, phenyl azide, azobenzene, aniline, nitrobenzene, acetic acid and derivatives of acetaldehyde. More recently the reduction of hexyl nitrate with hydrazine itself at room temperature, in the presence of a platinum or palladium catalyst, has been reported[5]; the products were nitrogen, nitrous oxide, and the parent alcohol. This latter reaction was said not to occur in the absence of the catalyst under the experimental conditions employed.

It has been found in this Laboratory that simple nitrate esters react with hydrazine at ordinary temperatures and without catalysts, but that the reactions are extremely slow unless high concentrations of the reactants are used.[6] With primary aliphatic nitrates, substitution[7] and reduction processes occur simultaneously, resulting in the formation of nitrate ion and alkylated hydrazines, and of nitrite ion, nitrogen, nitrous oxide, ammonia, hydrazoic acid, the parent alcohol and traces of aldehyde. The reduction process predominates when the nitrate ester reacts with excess hydrazine in the absence of added solvents; in aqueous alcoholic solution, the substitution process becomes increasingly important as the concentrations of reactants decrease. Ethyl, *n*-butyl and isoamyl nitrates all show this behavior.

The amount of gas produced was found to depend on the amount of excess hydrazine present, even in the absence of solvents. This variation is shown in Fig. 1. The maximum amount of gas obtained was 1.35 moles per mole of ethyl nitrate; this required at least a tenfold molar excess of hydrazine. In a typical experiment with 12 moles of hydrazine per mole of ethyl nitrate, the concentrations of nitrous oxide and ammonia were 7.0 and 8.7 mole per cent., respectively. The remainder of the gas, except for a trace of hydrazoic acid, was shown to be nitrogen by analysis in the mass spectrometer. Qualitative tests indicated the presence of azide ion in the solution. Nitrite ion formed rapidly and then disappeared as the reaction progressed, as shown in Fig. 2. Only 9% of the nitrate was found as nitrate ion. A small amount of ethanol was isolated and characterized; in similar experiments with *n*-butyl nitrate, the more easily isolable alcohol was obtained in yields in excess of 50%. A trace of aldehyde was obtained from one similar run using isoamyl nitrate, but none was found in any ethyl nitrate experiments. Ether-soluble basic oils were found which were presumed to be alkylated hydrazines, although the pure compounds could not be isolated. Attempts to characterize these as salts, particularly as oxalates, led to sharply melting ma-

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[1] Previous paper in series: R. T. Merrow, S. J. Cristol and R. W Van Dolah, THIS JOURNAL, **75**, 4259 (1953).

[2] Presented in part before the 123rd National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1953.

[3] R. Walther, *J. prakt. Chem.*, **53**, 433 (1896).

[4] E. Bamberger and O. Billeter, *Helv. Chim. Acta*, **14**, 219 (1931).

[5] L. P. Kuhn, THIS JOURNAL, **73**, 1510 (1951).

[6] It has been observed, qualitatively, that the rate of gas evolution is more rapid from β-chloroethyl nitrate, 1,3-dichloro-2-propyl nitrate, glyceryl trinitrate and diethylene glycol dinitrate than from unsubstituted aliphatic nitrates under the same conditions.

[7] The term "substitution" is used in this paper to denote a displacement reaction at the carbon atom bearing the nitrate group.

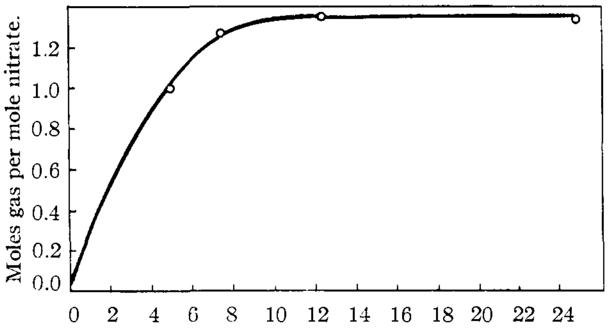

Fig. 1.—Variation in gas production with amount of excess hydrazine.

terials, but the analyses always indicated contamination with the salts of hydrazine itself. The formation of alkyl hydrazines was indicated by the fact that no olefin was found, thus ruling out β-elimination as the source of nitrate ion.

The formation of nitrite ion in these reactions apparently does not result from α-hydrogen elimination[8]

$$RCH_2ONO_2 \xrightarrow{\text{base}} RCH{=}O + HNO_2$$

since no appreciable amount of aldehyde is formed. It also is not formed *via* nitrate ion or the nitrite ester. Under the same conditions, sodium nitrate undergoes no reaction with excess hydrazine, as indicated by the absence of gas evolution and by the absence of any variation in the ultraviolet absorption spectrum. Neither ethyl nor *n*-butyl nitrite reacts with excess hydrazine to give nitrite ion. The major organic product of the reduction process, the parent alcohol, is not formed by reduction of the aldehyde, since, under the conditions used here, aldehydes or their hydrazones or azines are not reduced.[9]

The formation of nitrite ion and alcohol from nitrate esters previously has been shown to occur in electrolytic reduction[10] and in the reduction with alkaline hydrosulfides.[1] A mechanism similar to that postulated for the latter reaction can be formulated for the hydrazine reduction, as

$$\text{(a)}\quad RONO_2 + N_2H_4 \longrightarrow RO^- + H_2N{-}^+NH_2{-}NO_2 \quad (1)$$

$$\text{(b)}\quad H_2N{-}NH_2NO_2 + RO^- \rightleftarrows ROH + H_2N{-}NHNO_2$$

$$H_2N{-}NHNO_2 + N_2H_4 \longrightarrow \begin{cases} H_2NNHNHNH_2 + HNO_2 \\ \quad\text{I} \\ HN{=}NH + N_2H_5{}^+NO_2{}^- \\ \quad\text{II} \end{cases} \quad (2)$$

$$H_2N{-}NH{-}NH{-}NH_2 \longrightarrow N_2 + 2NH_3 \quad (3)$$

$$2HN{=}NH \longrightarrow \begin{cases} HN{=}NNHNH_2 \longrightarrow HN_3 + NH_3 \\ N_2 + N_2H_4 \end{cases} \quad (4)$$

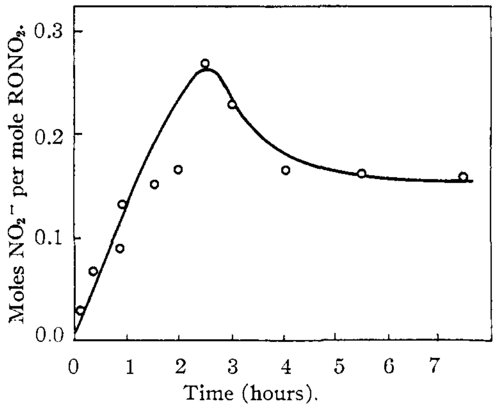

Fig. 2.—Variation of nitrite ion concentration during reaction of hydrazine with ethyl nitrate.

The reduction process almost certainly involves fission of the O–N bond,[11] since alkyl–oxygen cleavage gives nitrate ion which is not reduced under these conditions. Reaction 1 is an example of O–N cleavage, analogous to the acyl–oxygen fission which occurs in the hydrolysis of carboxylic esters. This type of cleavage of nitrate esters occurs in alkaline hydrolysis,[12] and in the nitration of aniline with ethyl nitrate in the presence of strong base.[13] Bamberger's attempted N-nitration of phenylhydrazine under the same conditions led only to oxidation products.[4] The only report of the formation of an *isolable* nitrohydrazine derivative was that of Picard and Boivin,[14] who nitrated dibenzoylhydrazine with acetyl nitrate. The formation of the unstable hydronitrogens, tetrazane (I) and diimide (II), and their decomposition by reactions 3 and 4 have been postulated as intermediate steps in other oxidations of hydrazine.[15] Stable azo compounds (*sym*-disubstituted diimides) have been obtained from the acetyl nitrate oxidation of some negatively disubstituted hydrazines.[14] In this Laboratory, methylhydrazine and ethyl nitrate were found to give methane (but no ethane) and nitrogen, which is suggestive of monomethyl diimide as an unstable intermediate.

The following reactions of nitrous acid, which are known to occur in aqueous solution,[16] may account for the disappearance of NO_2 in the later stages of the reduction of nitrate esters with excess hydrazine.

$$HNO_2 + N_2H_4 \longrightarrow NH_3 + N_2O + H_2O \quad (5)$$

$$HNO_2 + N_2H_4 \longrightarrow HN_3 + 2H_2O \quad (6)$$

$$HNO_2 + HN_3 \longrightarrow N_2 + N_2O + H_2O \quad (7)$$

Benzyl nitrate reacts with hydrazine predominantly by the substitution process, even in the absence of added solvent, giving a series of alkylated hydrazines as shown in Table I. Some reduction does occur, however, as evidenced by a lower yield

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[8] J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1193 (1952).

[9] While Wolff–Kishner reductions of aldehydes and ketones with hydrazine alone are reported, these require higher temperatures, and yield the hydrocarbon rather than the alcohol. In normal Wolff–Kishner reactions with alkaline catalysts, excess hydrazine is used to *prevent* formation of the alcohol. See D. Todd in R. Adams, Editor, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 378 ff.

[10] F. Kaufman, H. J. Cook and S. M. Davis, THIS JOURNAL, **74**, 4997 (1952).

[11] The type of fission involved is under further investigation by stereochemical means.

[12] S. J. Cristol, A. Shadan and B. Franzus, Abstracts of Papers, A.C.S. National Meeting, Kansas City, Mo., Spring, 1954, p. 20N.

[13] E. Bamberger, *Ber.*, **53B**, 2321 (1920); A. Angeli and M. V. Maragliano, *Atti accad. Lincei*, [5] **14**, II, 127 (1905), cited by H. J. Backer, *Sammlung Chem. und Chem. Tech. Vortrage*, **18**, 359 (1912).

[14] J. P. Picard and J. L. Boivin, *Can. J. Chem.*, **29**, 223 (1951).

[15] R. E. Kirk and A. W. Browne, THIS JOURNAL, **50**, 337 (1928).

[16] F. Sommer and H. Pincas, *Ber.*, **49**, 259 (1916).

of nitrate ion and the formation of small amounts of nitrite ion when no solvent is added. No gaseous products were obtained from this nitrate.

In addition to the benzylated hydrazines, benzal dibenzylhydrazine was isolated and identified. It is not certain whether this compound results from the reaction of benzaldehyde (formed by α-hydrogen elimination) with 1,1-dibenzylhydrazine, or from the oxidation of tribenzylhydrazine. Kenner and Wilson[17] showed that tribenzylhydrazine is very susceptible to oxidation, either by air or by other oxidants. The formation of benzaldehyde in the present experiments seems unlikely in view of the fact that no benzalazine was ever found.

t-Butyl nitrate undergoes carbon–carbon elimination almost exclusively, with the formation of isobutylene and hydrazine nitrate. No nitrogen or nitrogen oxides were detected by the mass spectrometer. A trace of a mixture of alkylated hydrazines was isolated as the nitrate salts. These results are in qualitative agreement with those of Baker and Easty,[8] who found the elimination reaction important in the alkaline hydrolysis of *t*-butyl nitrate, and with those of Lane,[18] who obtained only elimination products from the reaction of this ester with pyridine.

Experimental

All melting points are corrected. Microanalyses were performed by Elek Microanalytical Laboratories, Los Angeles, Calif., and by Mrs. L. B. Oliver of this Laboratory.

Materials.—Ethyl, *n*-butyl and isoamyl nitrates and *n*-butyl nitrite were obtained commercially and used without further purification. Ethyl nitrite was prepared by esterification of the alcohol.[19] Benzyl nitrate was made from the chloride and silver nitrate,[20] and *t*-butyl nitrate was prepared by esterification of the alcohol with 100% nitric acid.[20] The azines of acetaldehyde and *n*-butyraldehyde were made in the usual manner.[21]

It was found that anhydrous hydrazine, prepared by distillation from KOH, reacted to give the same products as the commercial 95% base, so the latter was used in most of the experiments described here.

Ultraviolet Absorption Spectra.—In order to determine whether nitrite ester, nitrate ion or aldehyde derivatives were intermediate reduction products, the ultraviolet spectra of various mixtures were taken, using 1-cm. quartz cells in a Cary recording spectrophotometer, model 11 MS. A mixture of equal volumes of 95% hydrazine and absolute ethanol was used as solvent. A solution of 0.04 ml. of either ethyl or *n*-butyl nitrate in 10 ml. of solvent showed initially only one absorption maximum near 270 mμ. As the reaction progressed, this peak disappeared completely, and maxima appeared and increased in height at 363 mμ (nitrite ion) and at 312 mμ (nitrate ion). When ethyl nitrite was used, in similar concentration, an initially strong peak near 270 mμ disappeared in time, but no new peaks appeared. This may have been due to loss of nitrite ester by volatilization. With *n*-butyl nitrite, there was a slight increase in the absorption maximum near 270 mμ, but no absorption developed in the 300–400 mμ range over a period of several days. In view of the facts (a) that no nitrite ion was detected in the nitrite ester reactions, and (b) that absorption at 270 mμ dropped to zero in nitrate ester reactions, but not in nitrite ester reactions, it was concluded that the nitrite ester was not an intermediate in the reduction of the nitrate ester.

The spectrum of a solution of sodium nitrate in the ethanolic hydrazine showed only one maximum at 312 mμ, and there was no change in the height of this peak over several days. A solution of 0.04 ml. of *n*-butyraldehyde in 10 ml. of solvent showed a strong absorption maximum near 270 mμ, which decreased somewhat over a three-day period, but which then remained constant at a high value. A reaction mixture containing 0.04 ml. of ethyl nitrate and 0.04 ml. of *n*-butyraldehyde in 10 ml. of solvent gave spectra which appeared to be the sum of the spectra of the two solutes separately; that is, the maxima appeared at 312 and 363 mμ and increased in height at about the same rate as with ethyl nitrate alone, and the strong absorption band at 270 mμ decreased in intensity with time, but stopped at about that value observed with the aldehyde alone, instead of dropping to zero. Thus the aldehyde (probably present as the hydrazone) apparently did not reduce the nitrate ester, nor was it reduced by the hydrazine.

When the hydrazine of the solvent was replaced by either acetaldehyde azine or *n*-butyraldehyde azine, there was no evolution of gas on addition of ethyl nitrate, and the spectra showed no change over a 24-hour period.

Analytical Procedures.—Nitrite ion concentration was determined by the Griess–Ilosvay method, essentially according to the procedure used by Kaufman.[11] The nitrite solution was diluted to 1 to 5×10^{-5} *M*, and 5 ml. of the diluted solution was treated with 0.5 ml. of a 1% solution of sulfanilic acid in 30% acetic acid and 0.5 ml. of a solution containing 0.1g. of α-naphthylamine in 250 ml. of 30% acetic acid. The mixture was allowed to stand for at least 10 minutes (but no longer than 45 minutes) and the optical density at 470 mμ was measured with a Beckman model DU spectrophotometer. Known solutions of sodium nitrite were used as standards. Nitrate esters and nitrate ion were shown not to interfere, and nitrite esters were shown by the ultraviolet spectra to be absent.

Nitrate ion was determined by extracting samples with ether and analyzing the aqueous layers by the spectrophotometric method of Holler and Huch.[22] Precipitation with nitron reagent also was attempted, but it was not possible to obtain good crystalline precipitates from solutions of high hydrazine concentration.

The gaseous products were analyzed qualitatively in the mass spectrometer (Consolidated Engineering Corp., Type 21-103), and by infrared absorption, using a Perkin-Elmer model 21 instrument. Quantitative estimation of nitrous oxide was made from the intensity of the infrared band at 7.7 μ. Ammonia was estimated from the bands at 9.67 and 11.21 μ.

Azide ion was detected by acidifying a small sample of solution with glacial acetic acid and adding a few drops of either silver nitrate or ferric chloride solution.[23] A white precipitate of silver azide or the deep red color of ferric azide indicated the presence of N_3^-.

Reactions were carried out, in general, by simply mixing the reactants and solvent (if any) in loosely stoppered volumetric flasks kept in a water-bath maintained near room temperature to avoid heating of the reaction mixture. Where gaseous products were to be collected, the nitrate ester was added to frozen hydrazine in an erlenmeyer flask connected by a side-arm through a cooling trap at 0° to a mercury-filled gas buret. The flask was stoppered and the system evacuated. The reactants were then allowed to warm to room temperature and react.

Hydrazine nitrate was isolated from the ether-insoluble portion of the reaction mixtures by partial removal of the excess hydrazine, addition of alcohol, and cooling. The various benzylated hydrazines and their salts were recovered from both ether-soluble and ether-insoluble fractions by removal of liquid at reduced pressure and fractional crystallization of the solid residue from ethanol–water mixtures. These products are listed in Table I.

The organic product of the reduction process was shown to be the parent alcohol by isolation from the ether-soluble fraction. Simple fractional distillation was sufficient for the isolation of butanol, but ethanol was more difficult to separate from the reaction mixtures. The procedure used involved addition of excess ethyl nitrate to the reaction

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[17] J. Kenner and J. Wilson, *J. Chem. Soc.*, 1108 (1927).

[18] E. S. Lane, *ibid.*, 1172 (1953).

[19] W. L. Semon and V. R. Damerell in A. H. Blatt, Editor, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 204.

[20] G. R. Lucas and L. P. Hammett, THIS JOURNAL, **64**, 1928 (1942).

[21] H. C. Barany, E. A. Braude and M. Pianka, *J. Chem. Soc.*, 1898 (1949).

[22] A. C. Holler and R. V. Huch, *Anal. Chem.*, **21**, 1385 (1949).

[23] F. Feigl, "Qualitative Analysis by Spot Tests," Second English Edition, 1939, Elsevier Press, Amsterdam; Nordemann Publishing Co., Inc., New York, N. Y., p. 185.

TABLE I

ORGANIC PRODUCTS ISOLATED FROM THE REACTION OF HYDRAZINE WITH BENZYL NITRATE

Compound	M.p., °C. Lit.[a]	M.p., °C. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
$C_6H_5CH_2N_2H_3 \cdot HNO_3$	..	172.5–173.5	45.40	56.24[b]	5.99	6.46[b]	22.69	17.76[b]
$(C_6H_5CH_2)_2N_2H_2 \cdot HNO_3$	..		61.07		6.23		15.26	
$(C_6H_5CH_2)_3N_2H \cdot HNO_3$	..	188–188.5	69.02	69.42	6.34	6.49	11.50	11.04
$(C_6H_5CH_2)_4N_2$	139	139–140	85.67	85.83	7.19	7.05	7.14	7.12
$(C_6H_5CH_2)_2N{-}N{=}CHC_6H_5$[c]	87	83–84	83.96	84.39	6.71	6.96	9.33	8.57

[a] Ref. 17. [b] This analysis indicated a mixture of mono- and higher benzylated hydrazine mononitrates. A hydrochloride was obtained from this product, m.p. 213–215° dec. 1,2-Dibenzylhydrazine monohydrochloride has m.p. 215–217° dec. (A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 312 (1950)). [c] It was not possible to improve either the m.p. or the analysis of this product. Hydrolysis with HCl gave benzaldehyde and a hydrochloride, m.p. 198.5–199.5°; N, 11.34; reported (ref. 17) for 1,1-dibenzylhydrazine monohydrochloride, m.p. 202°; N (calcd.), 11.26.

mixture after completion of a reaction, immediate extraction with ether, and distillation of the ethanol–ethyl nitrate azeotrope from the ether-soluble fraction. The α-naphthylurethan was prepared directly from the azeotropic mixture. Butanol was characterized by boiling point, refractive index, and by derivatization as the α-naphthylurethan.

Attempts were made to detect aldehyde by refluxing the ether-soluble fractions with dilute HCl (to hydrolyze any hydrazones or azines) and adding 2,4-dinitrophenylhydrazine (DNP). A DNP derivative was obtained from one experiment with isoamyl nitrate and was shown to be that of isovaleraldehyde, m.p. and mixed m.p. 122–123°. No evidence of aldehyde formation was obtained from any experiments using *n*-butyl or ethyl nitrate.

Acknowledgment.—The authors are indebted to Dr. C. A. VanderWerf and Dr. Howard W. Kruse for some of the starting materials; to Dr. S. R. Smith for the mass spectra; and to R. H. Pierson for some of the infrared spectra. Thanks are also due to Kathryne B. Clifton and Mario J. Falbo for assistance in various phases of this investigation.

CHINA LAKE, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY AND THE LABORATORY FOR ORGANIC CHEMISTRY, UNIVERSITY OF AMSTERDAM]

Orientation in Aromatic Nitration Reactions[1]

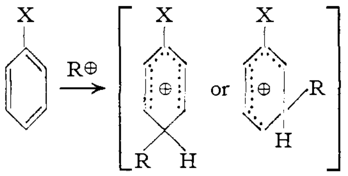
BY JOHN D. ROBERTS,[2,3] JANET K. SANFORD,[2,4] F. L. J. SIXMA,[5] H. CERFONTAIN[5] AND R. ZAGT[5]

RECEIVED MARCH 8, 1954

The isotope dilution method has been employed to determine isomer distributions in the nitration of chloro-, bromo- and iodobenzenes and the relative reactivity of iodobenzene with respect to benzene. For nitration at 25°, the following isomer distributions were found: chlorobenzene, *ortho* 29.6 ± 1.7%, *meta* 0.9 ± 0.0%, and *para* 69.5 ± 1.7%; bromobenzene, *ortho* 36.5 ± 1.7%, *meta* 1.2 ± 0.1%, and *para* 62.4 ± 2.8%; iodobenzene, *ortho* 38.3 ± 2.0%, *meta* 1.8 ± 0.3%, and *para* 59.7 ± 2.0%. The reactivity of iodobenzene relative to benzene at 25° was 0.13 in acetic anhydride and 0.22 in nitromethane. The degree of correlation of the nitration reactivities of benzene derivatives with Hammett σ-constants is discussed. Deviations from the Hammett relationship are interpreted in terms of important contributions of transition-state resonance.

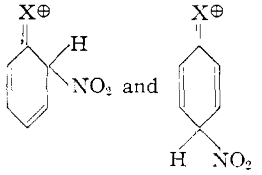
Introduction

Considerable disagreement exists as to the importance, in electrophilic aromatic substitution, of transition-state resonance interactions involving the orienting substituent groups and most easily discussed in terms of the customary pentadienate cation model (I) of the transition state.



I

Although Hammett's statement[6] that relative reactivities in the nitration of substituted benzenes parallel the σ-constants of the substituents would seem to exclude important resonance contributions of the following type for *o*- and *p*-substitutions



II

evidence for significant contributions of such resonance has long been accumulating. Kenner[7] found substantial differences in the charge at the *p*-position of a halobenzene when calculated from nitration rate data and from dipole moment data, respectively, attributed by him to transition state resonance during nitration. Transition state resonance involving the *p*-position also has been postu-

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[1] Supported in part by the joint program of the Office of Naval Research and the U. S. Atomic Energy Commission; also supported in part by a grant from the van't Hoff Fund of the Koninklijke Ned. Akademie van Wetenschappen. Presented before the Division of Organic Chemistry at the New York meeting of the American Chemical Society, September 13, 1954.

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[5] University of Amsterdam.

[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 198–199.

[7] G. W. Kenner, *Proc. Roy. Soc.*, **A185**, 119 (1946).