

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Kinetic Studies of Nitration with Nitronium Fluoroborate¹

By L. L. CIACCIO AND R. A. MARCUS²

RECEIVED NOVEMBER 8, 1961

Using nitronium fluoroborate as a nitrating agent, rates of nitration of nitrobenzene to *m*-dinitrobenzene were measured in methanesulfonic acid, in sulfuric acid and in acetonitrile. For comparison, the nitration rates were also determined with nitric acid in each of these solvents and with anhydrous nitric acid alone. The reaction was followed by polarographic analysis of quenched samples. Conditions for purification of the fluoroborate, analysis and preparation of kinetically reproducible methanesulfonic acid are described. The reaction is first order in nitrobenzene and first order in the nitrating agent (except for HNO₃ in CH₃SO₃H). Second order rate constants are about equal for the two nitrating agents in sulfuric acid and, when the HNO₃ data are extrapolated to zero HNO₃, in methanesulfonic acid. The rate constants in the two solvents are also comparable in magnitude. When a second order rate constant in anhydrous nitric acid is computed from the estimated NO₂⁺ concentration, its value at -13° is about the same as those observed in the above acidic solvents at 25°, and its approximate value at room temperature is appreciably greater. In acetonitrile, the rate constant with NO₂BF₄ is much less, in qualitative agreement with the negligible content of free NO₂⁺ in this medium as deduced from infrared spectra. The nitration rate with HNO₃ in acetonitrile is negligible. The study extends somewhat the range of solvents suitable for the investigation of medium effects on the attack of aromatics by NO₂⁺.

Introduction

Numerous studies support the belief that the nitronium ion is the effective nitrating agent in many nitrating systems.³⁻⁵ It is also well established now that the elimination of the hydrogen with substitution by NO₂⁺ is not rate determining, in the case of aromatics at least.^{4g,j,l} The reaction order is frequently complex, occasionally because the rate of NO₂⁺ formation is sometimes

slow,^{4d} but much more frequently because of complex preequilibria involving the nitronium ion. Accordingly, the kinetic study of the nitrating behavior of a nitronium salt was undertaken here. Such a salt, it would be expected, should be an unusually effective nitrating agent, capable of producing high reaction rates and high yields.

The existence of the nitronium ion in various nitronium salts of strong acids and their solutions has been established by a number of techniques,⁵ and its salts have been synthesized in a variety of ways, *e.g.*,⁶ recently, the synthesis of nitronium fluoroborate was reported^{8a,c,d}. The stability of this salt, the relative inertness of its anion and the ease of its synthesis prompted its use in the present kinetic study. Solutions of it in anhydrous nitric acid have been shown by infrared spectra to contain a considerable concentration of nitronium ion.^{5l}

The present paper reports kinetic studies with nitronium fluoroborate in a variety of solvents. The only previous studies are a detailed kinetic study with acetic acid as solvent⁷ and a measurement of nitration yields of many compounds.⁸ In addition to studies with nitronium fluoroborate, kinetic data for nitric acid were also obtained and are reported below for comparison, using a number of solvents, some of which are novel for nitration.

Analytical methods previously used to study rates of aromatic nitration include chemical analysis of product,^{4a} calorimetry,^{4b,j} analysis of residual nitric acid (sometimes checked by density measurement of the molten organic material),^{4c,e,f,k,j} dilatometry,^{4d,i} isotopic analysis^{4g,l} and ultraviolet spectroscopy.^{4a,o} Several of these studies involved nitration of nitrobenzene.^{4a,b,d-f,k} Because of the novelty of the nitrating agent and of some of the solvents, polarography was used rather than measurement of some physical property, since this method is capable of giving excellent

(1) Abstracted from a doctoral thesis to be submitted by L. Ciaccio in partial fulfillment of the degree of Doctor of Philosophy, Polytechnic Institute of Brooklyn. Microfilm copies will be available from University Microfilms, Ann Arbor, Michigan. Presented in part at the 133rd National Meeting of the American Chemical Society in San Francisco, April 1958.

(2) Alfred P. Sloan Fellow.

(3) Reviews: (a) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Academic Press, New York, N. Y., 1959, Chap. 5; (b) C. K. Ingold "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, pp. 269-288; (c) R. J. Gillespie and D. J. Millen, *Quart. Revs.* (London), **2**, 277 (1948). The last two reviews contain many references to the earlier literature omitted below.

(4) Kinetic studies: (a) H. Martinsen, *Z. phys. Chem.*, **50**, 385 (1904); **59**, 605 (1907); (b) F. H. Westheimer and M. S. Kharasch, *J. Am. Chem. Soc.*, **68**, 1871 (1946); (c) G. M. Bennett, J. C. D. Brand, D. M. James, T. G. Saunders and G. Williams, *J. Chem. Soc.*, 474 (1947); (d) E. D. Hughes, C. K. Ingold and R. I. Reed, *ibid.*, 2400 (1950); (e) T. G. Bonner, M. E. James, A. M. Lowen and G. Williams, *Nature*, **163**, 955 (1949); (f) A. M. Lowen, M. A. Murray and G. Williams, *J. Chem. Soc.*, 3318 (1950); (g) L. Melander, *Arkiv. Kemi*, **2**, 211 (1950); (h) A. H. Vroom and C. A. Winkler, *Can. J. Research*, **28 B**, 701 (1950); (i) C. A. Bunton and E. A. Halevi, *J. Chem. Soc.*, 4917 (1952); (j) T. G. Bonner, F. Bowyer and G. Williams, *ibid.*, 3274 (1952), 2050 (1953); (k) R. J. Gillespie and D. Norton, *ibid.*, 971 (1953); (l) W. M. Lauer and W. E. Noland, *J. Am. Chem. Soc.*, **75**, 3689 (1953); (m) R. A. Marcus and C. A. Winkler, *Can. J. Chem.*, **31**, 602 (1953); (n) N. C. Deno and R. Stein, *J. Am. Chem. Soc.*, **78**, 578 (1956); (o) M. A. Paul, *ibid.*, **80**, 5329 (1958).

(5) Physical properties (Raman and infrared spectra, crystallography conductivity, and cryoscopy): (a) J. Chedin, *Ann. chim.*, **8**, 243 (1937), *Mem. serv. Chem. l'Etat* (Paris), **31**, 113 (1944); (b) R. J. Gillespie, J. Graham, E. D. Hughes, C. K. Ingold and E. R. A. Peeling, *Nature*, **158**, 480 (1946); (c) G. M. Bennett, J. C. D. Brand and G. Williams, *J. Chem. Soc.*, 869, 875 (1948); (d) E. G. Cox, G. A. Jeffrey and M. R. Truter, *Nature*, **162**, 259 (1948); (e) J. Chedin and S. Feneant, *Compt. rend.*, **229**, 115 (1949); (f) P. E. Grison, K. Ericks and J. L. de Vries, *Acta Cryst.*, **3**, 290 (1950); (g) R. J. Gillespie, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2552 (1950); (h) C. K. Ingold, D. J. Millen and H. G. Poole, *ibid.*, 2576 (1950); (i) D. J. Millen, *ibid.*, 2600, 2606 (1950); (j) R. Teranishi and J. C. Decius, *J. Chem. Phys.*, **22**, 896 (1954); (k) W. H. Lee and D. J. Millen, *J. Chem. Soc.*, 4463 (1956); (l) R. A. Marcus and J. M. Fresco, *J. Chem. Phys.*, **27**, 564 (1957); (m) A. Kent and R. A. Marcus, unpublished results; (n) W. J. Dunning and C. W. Nutt, *Trans. Faraday Soc.*, **47**, 15 (1951); (o) N. C. Deno, H. J. Peterson and B. Sacher, *J. Phys. Chem.*, **65**, 199 (1961).

(6) (a) A. A. Woolf and H. J. Emeleus, *J. Chem. Soc.*, 1050 (1950); (b) D. R. Goddard, E. D. Hughes and C. K. Ingold, *ibid.*, 2559 (1950); (c) M. Schmeisser and S. Blischer, *Z. Naturforsch.*, **7b**, 583 (1952); (d) E. E. Aynsley, G. Hetherington and P. L. Robinson, *J. Chem. Soc.*, 1119 (1954).

(7) L. L. Ciaccio, M. S. Thesis, Polytechnic Institute of Brooklyn, June 1956, *J. Am. Chem. Soc.* (to be submitted). (Presented at A. C. S. Meeting, April, 1958.)

(8) G. Olah, S. Kuhn and A. Mlinko, *J. Chem. Soc.*, 4257 (1956). For studies of related interest, *cf.* G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **80**, 6541 (1958).

identification of the products formed and an unambiguous estimate of their amount.

Experimental

Synthesis and Purification of NO_2BF_4 .—The method of Emeleus and Woolf^{9a} was used to synthesize the nitronium compound. However, the synthesis was performed in the present work in a Pyrex flask at -10° , using 0.025 mole of B_2O_3 , 20 ml. of Br_2 , 0.10 mole of BrF_3 (ca. 50% excess), and 0.10 mole of NO_2 (ca. 100% excess). The average yield was 95% of the theoretical based on B_2O_3 .

We found that the compound sublimes readily under vacuum and this method of purification produces crystals of NO_2BF_4 . It was also observed that heating the material instead at atmospheric pressure at 150° removed adsorbed yellow impurities and formed powdered NO_2BF_4 . All batches of the latter gave similar kinetic results. The second method was the one used in the present paper. Mr. R. Alonso of this Laboratory showed that similar rate constants were obtained with both preparations. (He used anhydrous methanesulfonic acid as solvent.) The NO_2BF_4 was stored in a desiccator open to the atmosphere *via* P_2O_5 traps.

Analysis of Purity.—Analysis of nitronium salt purified by the first method gave 10.6% N, 8.2% B and 57.2% F and the second method gave 10.0% N, 8.8% B and 55.4% F. (Calcd. for NO_2BF_4 , 10.6%, 8.2%, 57.2%, respectively). The analysis indicated 2% unreacted boric oxide present in the latter sample. Spectrographically, the silicon content was found to be less than 0.1%, showing negligible contamination by any nitronium hexafluorosilicate formed through attack on the Pyrex vessel. Nitrogen content was determined by use of a modified Kjeldahl method for alkali nitrates^{9,10} after adapting it to a microtechnique.⁷ The per cent. of fluorine was measured indirectly by completely hydrolyzing the nitronium fluoroborate using calcium chloride¹¹ and titrating the acid liberated. This total acidity, corrected for the nitric acid formed, gave the fluorine content. The boron content was obtained by titrating the neutralized hydrolysis products of nitronium fluoroborate in the presence of mannitol or glycerol.¹²

All other batches were analyzed by nitrogen determination^{7,9,10} and showed 95–98 mole per cent. nitronium fluoroborate.

Preparation of Other Materials.—Porous boric oxide¹³ was prepared from reagent grade amorphous boric acid. Nitrogen dioxide was refluxed over P_2O_5 and stored over it at -10° . Reagent grade bromine was dried over P_2O_5 and distilled. Other reagents needed for the preparation of the nitronium compound were used as obtained. Reagent grade nitrobenzene and *m*-dinitrobenzene were purified by the usual methods of distillation and recrystallization, respectively.

Nitric acid was prepared by mixing at 0° 1 part by volume of 99% fuming nitric acid and 2 parts of concentrated sulfuric acid each previously cooled to 0° . Distilled at 5 mm. and collected at -78° , the anhydrous nitric acid was stored in the dark at -78° . The total acidity was assayed as 99.98% nitric acid by weighed buret titration. The nitrous acid content was determined colorimetrically to be 0.004 *M*.¹⁴

Methanesulfonic acid (Eastman Kodak P6320) was purified by adding 20 g. of reagent grade P_2O_5 to 500 ml. of the acid, stirring the mixture at 100° for 30 minutes and distilling *in vacuo* at about 160 – 170° and 4 mm. The colorless liquid acid was obtained, occasionally preceded by some solidified anhydride. Methanesulfonic acid anhydride

was prepared by distilling methanesulfonic acid containing excess P_2O_5 using a molar ratio, $\text{P}_2\text{O}_5/\text{CH}_3\text{SO}_3\text{H}$, of 0.18. The distillation was performed at ca. 160° and 5.5 mm. Before use in nitration, methanesulfonic acid containing added 1 *M* anhydride was kept at 120 – 130° for 150 minutes, protected from moisture.¹⁵ A slight darkening sometimes occurred during heating.

Reagent grade concentrated sulfuric acid was mixed with reagent grade 30% fuming sulfuric acid to obtain a solvent containing a known low concentration of water or SO_3 , as determined by titration with weighed burets.

Reagent grade acetonitrile was dried over P_2O_5 ¹⁶ and found by Karl Fischer titration to contain less than 0.001 *M* water.

Solubility of NO_2BF_4 in Various Solvents.—This compound was found in this study to be soluble in methanesulfonic acid (<0.7 *M*), sulfuric acid, nitric acid, acetic acid and acetonitrile (<0.3 *M*). It was but slightly soluble or insoluble in chloroform, carbon tetrachloride, nitromethane, trifluoroacetic acid, dimethyl sulfate and formamide. It reacted violently with benzene to form a number of nitrated products and with acetic anhydride, dimethyl formamide and dimethyl sulfoxide. The rate of solution of powdered and crystalline NO_2BF_4 in methanesulfonic acid was very different, the former being rapidly soluble (typically, it dissolved in ten minutes) and the latter only being slowly soluble (typically, dissolved in 45 minutes).

Preparation of Nitration Solutions and Procedure.—Equal volumes of a solution of nitrobenzene in the solvent and of the nitrating agent in the solvent were prepared and placed in a closed vessel in a P_2O_5 desiccator in an air bath at 24° . Within ten minutes of the preparation of the latter solution, aliquots were mixed and the reaction rate was followed by analysis of quenched samples. *m*-Dinitrobenzene was measured polarographically in a pH 9.2 buffer medium.¹⁷

Samples of 1 ml. (for 0.01 *M* $\text{C}_6\text{H}_5\text{NO}_2$, 2 ml. for lower concentrations) were removed by pipet, quenched as described below and neutralized to a pH of 9.2. During neutralization the solution temperature was not allowed to exceed 35° . *m*-Dinitrobenzene was measured in the neutralized solution at 25° using a Sargent Model XXI polarograph in conjunction with a specially constructed semimicro H cell which requires a maximum of 5 ml. of solution. The *I* value¹⁸ for *m*-dinitrobenzene ($I = i_d/\text{Cm}^{1/2}t^{1/2}$) in a borate buffer was essentially the same for NH_3 – $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 systems used below and essentially unaffected by any acetonitrile or methanesulfonate ion present.

Quenching Procedures.—When the solvent was methanesulfonic acid or acetonitrile, the quenching solution used was 5 ml. of 0.3 *M* borate buffer (pH 9.2), kept in a 25 ml. volumetric flask at 0° . After quenching, the pH was adjusted to 9.2 by addition of strong NaOH followed by 2 ml. of denatured (3A) ethanol and dilution to 25 ml. with borate buffer.

When the solvent was sulfuric acid, each 1 ml. solution was quenched in a solution of 2 ml. of 3A ethanol and 1 ml. of water in a 25 ml. volumetric at -40° . The solution was then diluted with cold water adjusted to pH 9.2 with concentrated ammonia and diluted with water to 25 ml.

Procedures with Anhydrous Nitric Acid.—When the solvent was anhydrous nitric acid, the reaction was performed several times at -13° in a Dewar. Nitrobenzene was added in a sealed sample bulb to nitric acid at the desired temperature and crushed with a stirring rod, but for the higher con-

(15) In our early work using methanesulfonic acid alone, different batches gave variations in rate of the order of 40%. It was inferred from specially designed kinetic experiments that water and anhydride readily coexist. In those experiments, a comparatively low nitration rate was found when water and anhydride were both added to the methanesulfonic acid before addition of NO_2BF_4 . In other experiments without added anhydride, the second order rate constant (k_2 in Table I) fell from 0.78 to 0.56 and to 0.17 when 0.20 *M* and 0.40 *M* H_2O were added to the methanesulfonic acid-excess anhydride system. In more recent unpublished work of Mr. R. Alonso of this Laboratory, even greater precautions were taken to insure anhydrous conditions, including the execution of experiments in a dry box. Rate constants in the methanesulfonic acid-anhydride system were then almost 50% higher than under the less rigorous conditions.

(16) P. Walden and E. J. Birr, *Z. phys. Chem.*, **144A**, 269 (1929).

(17) J. Pearson, *Trans. Faraday Soc.*, **44**, 683 (1948).

(18) I. M. Kolthoff and J. Lingane, "Polarography," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1952, p. 381.

(9) I. M. Kolthoff and V. A. Stenger, "Volumetric Methods of Analysis," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1947, page 172.

(10) W. E. Dickinson, *Anal. Chem.*, **26**, 777 (1954).

(11) S. V. Tatarskie, E. N. Kornilova and F. A. Sheinina, *Trudy Komissii, Anal. Khim., Akad. Nauk, S. S. S. R.*, **3**, 287 (1951); abstracted in *C. A.*, **47**, 2642i (1953).

(12) H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, page 235.

(13) W. C. Fernelius, Ed. "Inorganic Syntheses," Vol. II, McGraw-Hill Book Company, New York, N. Y., 1946, page 22.

(14) "Standard Methods for the Examination of Water, Sewage and Industrial Wastes," 10th Ed., American Public Health Association, New York, N. Y., 1955, pp. 153–155.

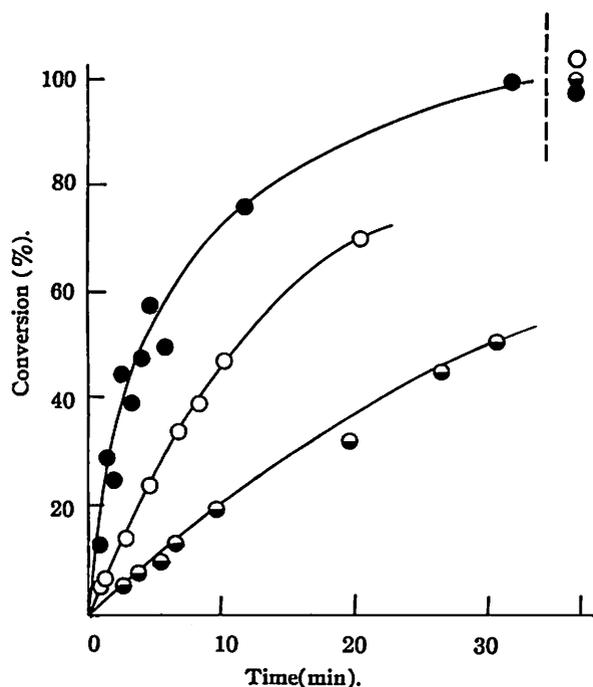


Fig. 1.—Typical kinetic curves for nitration of nitrobenzene with nitronium fluoroborate: ●, in sulfuric acid (expt. 162); ○, in methanesulfonic acid (expt. 132); ●, in acetonitrile (expt. 82).

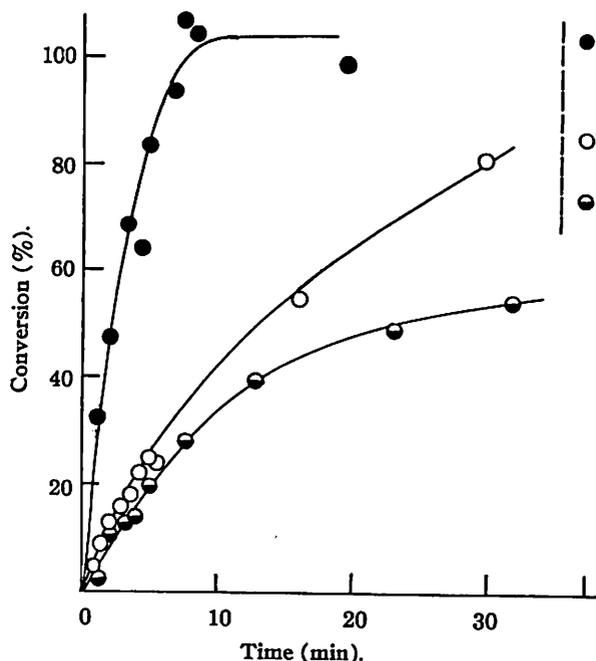


Fig. 2.—Typical kinetic curves for nitration of nitrobenzene with nitric acid; ●, in anhydrous nitric acid (expt. 189); ○, in methanesulfonic acid (expt. 179); ●, in sulfuric acid (expt. 190). For expt. 189, the time scale should be divided by a factor of two ($\tau_{1/2} = 1$ min.)

centration of nitrobenzene it was added with a micropipet. Aliquots were quenched in 5 ml. of water (0°), adjusted to pH of 9.2 with concentrated ammonia followed by addition of 2 ml. of (3A) ethanol and diluted to 25 ml. with water.

Results

Initial rates were measured from data at 5–30% reaction, the solution always containing excess

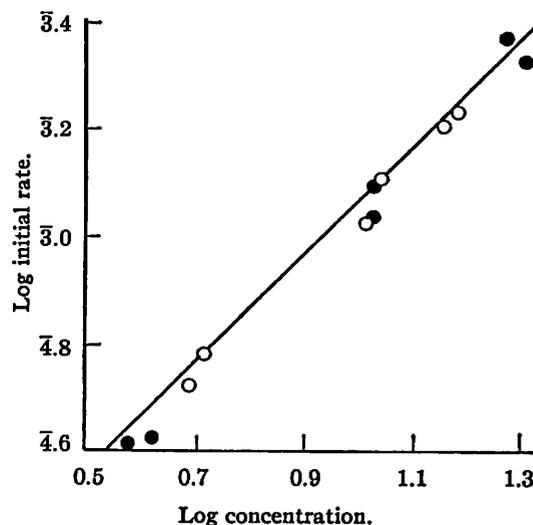


Fig. 3.—Log-log plots to determine reaction order: ○ (ϕ NO₂) is constant (corrected slightly to 0.01 M when necessary) and abscissa is $2 + \log(\text{NO}_2\text{BF}_4)$; ●, (NO₂BF₄) is constant (corrected slightly to 0.1 M) and abscissa is $3 + \log(\text{C}_6\text{H}_5\text{NO}_2)$. For both cases the straight line is the theoretical line of unit slope.

nitration agent.¹⁹ Typical kinetic curves are given in Figs. 1 and 2. Some fifty such kinetic curves were obtained in this study, and in each of these curves some ten reaction time points were determined.

The reaction was found to be first order in nitrobenzene and first order in nitronium fluoroborate in all solvents used in this paper, a result which contrasts with the odd behavior (fourth order with respect to NO₂BF₄) found in acetic acid medium.⁷ This kinetic behavior is illustrated in Fig. 3 for the solvent methanesulfuric acid containing added anhydride.

In the latter medium the yields and kinetic data obtained with NO₂BF₄ were excellently reproducible, more so than with sulfuric acid. The quenching problems in sulfuric acid were greater because of the higher heat of neutralization. Acetonitrile also proved to be an excellent solvent for high yields and reproducible data, though the rates were much less.

These and other results are summarized later in Table I, where second order rate constants determined from initial rates (k_2) and those determined from half-reaction times (in the presence of a large excess of NO₂BF₄ or HNO₃) $k_2' = 0.69/t_{1/2}(\text{NO}_2\text{X})$ are given. The average final yields, the concentration ranges used to test reaction order and the mean deviations in the k_2 's are also reported in Table I.

With nitric acid as nitrating agent, the reaction was first order in nitrobenzene in all solvents used, and first order in nitric acid when sulfuric acid was the medium. No nitration of nitrobenzene was observed using HNO₃ in acetonitrile. In methanesulfonic acid, the quasi-second order rate constant decreased with increasing nitric acid and appeared to reach a limiting value at high concen-

(19) For a detailed presentation of the data, cf. forthcoming Ph.D. thesis by L. Ciaccio.

TABLE I
 SUMMARY OF KINETIC DATA^a

Nitrating agent	Solvent	Variation in NO ₂ X (M) × 10	Variation in C ₆ H ₅ NO ₂ (M) × 100	Temp. (°C.)	Ave. yield (%)	No. of expts.	Mean <i>k</i> ₂ (M min.) ⁻¹	Mean <i>k</i> ₂ ' (M min.) ⁻¹	Mean devn. in <i>k</i> ₂
NO ₂ BF ₄	CH ₃ SO ₃ H	0.5-1.5	0.4-2	25	100	12	1.1	1.1	0.05
NO ₂ BF ₄	H ₂ SO ₄ ^b	.5-3	.4-2	23	85	6	0.42	0.46	.06
NO ₂ BF ₄	H ₂ SO ₄ ^c	.5-1	.4-1	23	90	5	.25	.32	.06
NO ₂ BF ₄	CH ₃ CN	1-2	2-4	21	100	3	.11	.11	.01
HNO ₃	CH ₃ SO ₃ H	0.5-20	0.4-2	24	90	9	(1.2) ^d	(1.2) ^d	..
HNO ₃	H ₂ SO ₄	0.3-1.0	0.4-2	23	85	5	0.46	0.44	.08
HNO ₃	HNO ₃	...	1-20	-13	100	2	1.0 ^e	1.2 ^e	.06
		...	1	21	100	1	...	~10 ^e	..
HNO ₃	CH ₃ CN	1-2	2	21	0	2	<2 × 10 ⁻⁵

^a Mean *k*₂ or *k*₂' denotes geometric mean: $\log \langle k \rangle = \sum_{i=1}^N (\log k_i) / N$. ^b 0.12 M H₂O. ^c 0.18 M SO₃. ^d Approximate value extrapolated to C_{HNO₃} = 0. ^e Based on an estimate of C_{NO₂}⁺ of 0.54 M at -13° and 0.35 M at 21° (see footnote 22). The initial rate in this medium at -13° was 3-fold greater than that reported previously under the same conditions but using a dilatometric analytical method supplemented by approximate chemical analysis (4d).

trations.²⁰ The value extrapolated to zero concentration is given in Table I where the other kinetic data for HNO₃ are also summarized.

Discussion

It is observed from Table I that the second order rate constants for nitronium fluoroborate and nitric acid are equal in sulfuric acid and, when the HNO₃ data are extrapolated to zero concentration of HNO₃, approximately equal in methanesulfonic acid. Of all the systems investigated in the present work, only the nitric acid-methanesulfonic acid system showed a dependence of the rate constant on concentration of nitrating agent, mainly a decrease with increase of HNO₃. This result can be explained by the observations that in forming NO₂⁺ only nitric acid produces water and that the methanesulfonic acid system is considerably more sensitive to added water than is the sulfuric acid system (*cf.* 15). The *k*₂-value for the HNO₃-H₂SO₄ system is comparable to the values of 0.4 and 0.6 obtained in refs. 4a and 4k under the same conditions of 100% H₂SO₄ and 25°.

In previous investigations, any comparison of *k*₂-values in different media was essentially limited to systems of varying H₂SO₄-H₂O content, since in other media the fraction of the nitrating agent present as NO₂⁺ was both small and unknown. It is a matter of interest and simplicity, therefore, that the values of this rate constant in anhydrous methanesulfonic acid and sulfuric acid are seen to be comparable in magnitude. The *k*₂-values need a small correction for extent of protonation of the nitrobenzene. If, as an extreme correction, the protonated form is taken to be unreactive, the rate constants in acid containing 0.12 M H₂O and 0.18 M SO₃ are raised from 0.42 and 0.25 M⁻¹ min.⁻¹ to approximately 0.48 and 0.51 M⁻¹ min.⁻¹, respectively.²¹ In methane-

sulfonic acid, where the insensitivity to added anhydride concentration suggests negligible protonation, the rate constant is 1.1 M⁻¹ min.⁻¹.

At -13° the nitration is especially rapid in anhydrous nitric acid, the half-reaction time being 1.0 minutes. However, the concentration of NO₂⁺ in this solvent is unusually high.²² The *k*₂-value computed on the basis of 0.54 M NO₂⁺ is 1.0 M⁻¹ min.⁻¹ at -13°. The half-reaction time at 21° was so low (~0.2 min.) that only a rather inaccurate *k*₂ (~10 M⁻¹ min.⁻¹) was estimated at that temperature.

These data for anhydrous nitric acid solvent may be compared with those obtained for 90% H₂SO₄ where the value of *k*₂ is a maximum in the H₂SO₄-H₂O system. From data^{4b} at 5°, 20° and 40°, *k*₂ can be estimated to be about 0.1 at -13° and 2.8 M⁻¹ min.⁻¹ at 21°, values which are substantially lower than in the anhydrous nitric acid system. The medium effect in the H₂SO₄-H₂O system is qualitatively understood^{4d,k} but with the present extension of solvent media further investigation could be made.

The absence of nitration by nitric acid in the poorly-ionizing acetonitrile is not unexpected. Again, the low rate of nitration using nitronium fluoroborate is consistent with observations of infrared spectra.^{5m} In the latter study the spectrum of an NO₂BF₄-CH₃CN system showed no significant amount of NO₂⁺, in contrast with the behavior of anhydrous nitric acid in the presence and absence of NO₂BF₄.^{5l}

Acknowledgments.—The authors would like to express their appreciation to Chas. Pfizer and Co., Inc., and to its Analytical Department for the use of their laboratory facilities. R. A. M. is indebted to the Alfred P. Sloan Foundation and to the National Science Foundation for fellowship awards.

(20) The *k*₂ values were 0.83, 0.55, 0.44, 0.20, 0.12 and 0.13 when the HNO₃ concentration in methanesulfonic acid was 0.51, 1.02, 1.53, 5.1, 10.2 and 19.2 M, respectively.

(21) *Cf.* basicity constants: J. C. D. Brand, W. C. Horning and M. B. Thornley, *J. Chem. Soc.*, 1374 (1952); *cf.* R. J. Gillespie and C. Solomons, *ibid.*, 1796 (1957).

(22) Cryoscopic results indicate 0.72 M at -40° (*cf.* 5k for references, *z.g.* 5n). Conductivity data indicate 0.61 and 0.51 M at -20° and -10°, respectively,^{5k} and 0.35 M at 25° (*cf.* 5k based on data of ref. 23). This last value compares with one of 0.2 M at 25° based on the effect of NO₂BF₄ on the infrared spectrum of HNO₃,^{5m} *cf.* 5l

(23) E. G. Taylor, M. L. Line and A. G. Follows, *Can. J. Chem.*, 29, 439 (1951).