as hypoiodous acid as the effective iodinating agent. A more complete study[54] gave the empirical result

$$\text{rate} = k_0'[\mathrm{PhOH}][\mathrm{I_2}]/[\mathrm{H^+}][\mathrm{I^-}] + k'_{\mathrm{HA}}[\mathrm{PhOH}][\mathrm{I_2}][\mathrm{HA}]/[\mathrm{H^+}]^2[\mathrm{I^-}] \quad (28)$$

where HA is a buffer acid such as acetic acid. The first term was interpreted as involving attack of HOI upon un-ionized phenol or alternatively I^+ (or H_2OI^+) upon phenoxide ion while the second term involved attack of acyl hypohalite upon phenoxide ion (or a general acid-catalyzed attack of hypoiodous acid upon phenoxide ion). We wish to point out that equation 28 is just the kinetic form which would be expected for mechanism III′ (involving iodine in place of bromine) with steps 16′ and 17′ essentially at equilibrium and, therefore, with the second right-hand term of equation 27 small relative to the first. The first right-hand term of equation 28 would then result from water being the general base which accepted the proton of step 19′ while the second term would involve the base A^- conjugate to the buffer acid. Moreover if mechanism III′ corresponds to the true mechanism of halogenation of phenol, then molecular iodine is seen to be the effective iodination agent. This iodinating agent has been shown to be responsible for the iodinolysis of *p*-methoxybenzeneboronic[55] acid in aqueous solution at iodide ion concentrations of 0.1 to 0.5 *M* and is apparently responsible for the exchange reaction between radioactive iodine and diiodotyrosine.[56]

At extremely low iodide concentrations such as are maintained by excess silver ion, the hypoiodous acidium ion (or iodinium ion) is probably the effective iodinating agent[57]; our question is whether in solution of high or moderately high iodide ion concentration the concentration of the hypoiodous acidium ion is sufficiently great to compete successfully with the much larger concentration of molecular iodine.[58] A final answer to this question for phenol must await a study of the kinetics of iodination to much lower iodide ion concentration or, perhaps better, a study of a possible hydrogen isotope effect here as a function of the iodide ion concentration. If mechanism III′ can be shown to apply to the kinetics of the iodination of phenol,[59] then probably a similar mechanism holds for the iodination of aniline.[60]

Acknowledgments.—The authors are indebted to the Graduate School for a fellowship to U. V. H. which made part of this work possible and to Dr. Jack Hine for helpful discussions.

ATLANTA, GEORGIA

---

[54] B. S. Painter and F. G. Soper, *J. Chem. Soc.*, 342 (1947); see also E. Berliner, THIS JOURNAL, **73**, 4307 (1951).

[55] H. G. Kuivila and R. M. Williams, THIS JOURNAL, **76**, 2679 (1954).

[56] A. H. Zeltmann and M. Kahn, *ibid.*, **76**, 1554 (1954).

[57] D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 3694 (1950); I. R. L. Barker and W. A. Waters, *ibid.*, 150 (1952); R. P. Bell and E. Gelles, *ibid.*, 2734 (1951).

[58] For a similar and more detailed argument concerning the reaction of oxalic acid with bromine *versus* hypobromous acidium ion see Y. Knoller and B. Perlmutter-Hayman, THIS JOURNAL, **77**, 3212 (1955).

[59] A somewhat similar mechanism has been considered for the iodination of 2,4-dichlorophenol but without appreciable experimental confirmation (J. E. Taylor and M. I. Evans, *Ohio J. Sci.*, **53**, 37 (1953)).

[60] E. Berliner, THIS JOURNAL, **72**, 4003 (1950).

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, PENNSYLVANIA STATE UNIVERSITY]

Carbonium Ions. III. Aromatic Nitration and the C_0 Acidity Function[1]

BY N. C. DENO AND RICHARD STEIN

RECEIVED SEPTEMBER 8, 1955

The rates of aromatic nitrations have been studied as a function of sulfuric acid concentration.

The work reported in this paper is part of the third step in a series of investigations carried out in aqueous sulfuric acids whose ultimate goal is to determine whether or not aliphatic tertiary alkyl cations exist as reaction intermediates. The first step in the program was to evaluate an acidity function (C_0), defined by eq. 1, where pK_{R^+} is the negative logarithm of the equilibrium constant for eq. 2.

$$C_0 = (pK_{R^+}) + \log\,(c_{\mathrm{ROH}}/c_{\mathrm{R^+}}) \quad (1)$$

$$\mathrm{H_2O} + \mathrm{R^+} = \mathrm{ROH} + \mathrm{H^+} \quad (2)$$

The second step was to test the generality of eq. 1 with data from a variety of equilibria in aqueous sulfuric acid. These two steps were accomplished in the initial paper of the series[2] in which a number of triaryl, diaryl and monoaryl groups were used for "R."

The third step in the program involved testing the generality of eq. 3 with kinetic data from appropriate acid-catalyzed reactions of the type of eq. 4 in which the group R was varied as widely as possible. Equation 3 follows directly from reaction path 4 if eq. 5 is valid.[2] In eq. 5, R^+ on the right-hand side of the equation represents the cations used to evaluate C_0 and R on the left-hand side refers to the same R as in reaction path 4. The superscript ($\neq$) in eq. 5 signifies the transition state for path 4, and "*f*" is an activity coefficient.

$$\log k = -C_0 + \text{constant} \quad (3)$$

$$\mathrm{ROH} + \mathrm{H^+} = \mathrm{H_2O} + \mathrm{R^+} \xrightarrow[\text{rate determining}]{+\ \mathrm{A}} \text{products} \quad (4)$$

$$\mathrm{d}\log\,(f_{\mathrm{A}} f_{\mathrm{ROH}}/f^{\neq})\mathrm{d}\ \%\ \mathrm{H_2SO_4} = \mathrm{d}\log\,(f_{\mathrm{ROH}}/f_{\mathrm{R^+}})/\mathrm{d}\ \%\ \mathrm{H_2SO_4} \quad (5)$$

The fourth step can be undertaken if eq. 3 proves satisfactory for a wide variety of R groups. This

---

[1] Grateful acknowledgment is made of the support of this research by a grant from the Petroleum Research Fund of the American Chemical Society.

[2] N. Deno, J. J. Jaruzelski and A. Schriesheim, THIS JOURNAL, **77**, 3044 (1955).

step would be to use eq. 3 as a diagnostic test for alkyl cations. *If kinetic data for an acid-catalyzed reaction of an alcohol followed eq. 3, it would be evidence that the t-alkyl cation was a reaction intermediate.*

Aromatic Nitration.—The nitration of benzene and several other aromatic compounds has been shown to proceed through reaction scheme 6.[3] Since this is of the same type as reaction scheme 4, kinetic data on nitration were an excellent test of the generality of equations 3 and 5, particularly since NO_2^+ is so different from the large aromatic cations that were used to evaluate C_0.

$$\mathrm{HNO_3 + H^+ = H_2O + NO_2^+} \xrightarrow[\text{rate determining}]{+\text{ subst. benzene}} \text{products} \qquad (6)$$

We have now studied the rates of nitration of methoxybenzene (anisole), benzene, fluorobenzene, chlorobenzene, bromobenzene and benzonitrile. The progress of the nitrations was followed spectroscopically since in each case a wave length was found at which the nitroaromatic absorbed while the absorption due to the reactants was negligible. The wave lengths used and the range of sulfuric acid concentrations studied are recorded in Table I.

TABLE I

RATE CONSTANTS FOR NITRATION OF SUBSTITUTED BENZENES

% H_2SO_4	Concentrations Reactant[a] (initial)	Concentrations Product[b] (final)	Ratio $\frac{\text{Col. 3}}{\text{Col. 2}}$	k^c ($\times 10^3$)
	Methoxybenzene (anisole)[f]			
62.80	0.312	*d*		30
59.59	.307	*d*		4.0
57.30	.352	0.890	2.53	0.98
53.54	.351	.875	2.50	.11
49.54	.373	.951	2.55	.015
45.25	.398	.988	2.48	.0020
41.30	.403	*d*		.00040
	Benzene			
69.09	0.820	0.748	0.91	
67.96	.769	.590	.77	26
66.92	.782	.701	.90	13
65.76		.660		2.9
64.17		.552		1.5
61.57	.965	.870	.90	0.14
59.48	.970	.890	.92	.042
57.30	.965	.890	.93	.014
54.01	.466	*e*		.0019
51.10	.504	*e*		.0004
	Fluorobenzene			
69.96	0.310	0.335	1.1	13
68.45	.152	.118	0.78	7.0
67.96	.246	.195	.79	4.0
66.40	.386	.330	.86	0.99
64.36	.395	.315	.80	.20
62.80	.390	.360	.92	.053
59.59	.542	*e*		.008
57.30	.445	*e*		.002
54.01	.560	*e*		.0004
	Chlorobenzene			
71.98	0.558	0.404	0.73	47
69.96	.185	.114	.62	7.7
68.45	.510	.243	.48	3.0
67.96	.655	.282	.43	1.70
64.36	.540	.240	.44	0.084
62.80	.166	.082	.49	.027
59.59	.521	*e*		.0025
57.04	1.06	*e*		.0007
	Bromobenzene			
71.98	0.307	0.623	2.03	45
69.96	.113	.256	2.26	7.3
68.45	.335	.467	1.43	2.7
67.96	.327	.471	1.44	1.60
64.36	.258	.385	1.49	0.072
62.80	.175	.250	1.43	.023
59.59	.609	*e*		.003
57.04	.495	*e*		.0007
	Benzonitrile			
87.0	0.343	0.087	0.254	
85.0	.370	.096	.259	9.0
84.0	.522	.134	.256	3.5
83.0	.300	.073	.243	1.5
82.0	.300	.072	.240	0.51
81.0	.486	*e*		.19
80.0	.237	*e*		.09
80.0	.652	*e*		.11

[a] In all runs the concentration of nitric acid was 0.61 mole/liter. The values listed in the second column are 26/25 times the initial concentration of benzene or substituted benzene as measured by the initial optical density. The factor 26/25 occurs to correct for the dilution due to the nitric acid, which was subsequently added. The wave lengths used to measure this initial concentration were methoxybenzene, 270 mμ; benzene, 260 mμ; fluorobenzene, 260 mμ; chlorobenzene, 222 mμ (1.7 mm. slit width); bromobenzene, 230 mμ (1.4 mm. slit width); and benzonitrile, 270 mμ. [b] This is the final concentration of product as measured by the final reading of the optical density. The wave lengths used were 370 mμ for nitrobenzene, 360 mμ for the mononitromethoxybenzenes and 340 mμ for the others. [c] The units of the rate constant, k, were sec.$^{-1}$ times (moles of substituted benzene/liter)$^{-1}$. Natural logarithms were used. [d] The final reading gave a value for the ratio (column 4) of 3.2 at 62.80% H_2SO_4 and 2.9 at 59.59% H_2SO_4. We had a choice of two different assumptions to use in order to calculate an approximate value for the rate constant. First was to accept the increase in the ratio as meaning that the extinction coefficient of the mononitromethoxybenzenes had unaccountably increased at these higher acid concentrations. Second was to assume that some colored impurity or by-product was causing the apparent increase in extinction coefficient and to realize that we could better approximate the true rate constant for nitration by calculating the final absorption using the initial concentration of reactant and an average value of measured ratios. We chose this latter method principally because the resulting values of d log k/d % H_2SO_4, listed in Table III, then gave close agreement to the values determined for the other reactants in the 57.5–62.5% range of sulfuric acid concentrations. [e] The final value was computed from the initial concentration of reactant times a weighted average of the measured ratios in column 4. [f] The rate constants were corrected for lowering of HNO_3 concentration due to ionization of HNO_3 to H^+ and NO_3^-. A value of -2.80 was chosen for the pK of the equilibrium, $NO_3^- + H^+ = HNO_3$, because it resulted in the best fit between values of d log k/d % H_2SO_4 and $-$d C_0/d % H_2SO_4 listed in Table III. It was also assumed that H_- and H_0 had a constant difference in this 40–55% H_2SO_4 region which is probable in view of the small changes in activity coefficients (ref. 10).

From the demonstrated reaction path (eq. 6) eq. 7 can be derived as the rate law. In this work, ni-

---

[3] The excellent work of Melander, Westheimer, Ingold, Gillespie, Williams and others has been reviewed by R. J. Gillespie and D. J. Millen, *Quart. Rev.*, **2**, 277 (1948).

tric acid was always used in excess. The linear nature of the plots of time against the logarithm of the concentration of substituted benzene confirmed that the concentration of substituted benzene enters as the first power in the rate expression. In nearly all of the runs data were obtained to 90–99% completion with no detectable deviation from first-order kinetics. In order to indicate the type of data recorded, one-third of the points from two typical runs are summarized in Table II.

$$-\mathrm{d}c_{\mathrm{A}}/\mathrm{d}t = kc_{\mathrm{A}}a_{\mathrm{HNO_3}}(a_{\mathrm{H^+}}/a_{\mathrm{H_2O}})(f_{\mathrm{A}}/f^{\ddagger}) \qquad (7)$$

TABLE II

SAMPLE CALCULATIONS OF RATE CONSTANTS FOR NITRATION

Time (sec.) × 10^{-3}	Concn. of[a] reactant	% Completion	k[b] × 10^3
Methoxybenzene, 53.54% H_2SO_4			
0.0	0.878	0	
2.640	.707	20	0.0810
5.400	.576	35	.0807
8.880	.430	51	.0801
15.120	.260	70	.0804
37.380	.045	95	.0794
49.200	.010	99	.09
Bromobenzene, 67.96% H_2SO_4			
0.0	0.471	0	
.300	.280	41	1.73
.420	.232	51	1.69
.600	.177	62	1.63
.900	.115	76	1.57
1.800	.032	93	1.5
2.760	.005	99	1.6

[a] These values are the final optical density minus the optical density at time indicated. The wave lengths used are listed in footnote *b* of Table I. [b] The units are the same as in Table I.

The identity of the nitrobenzene produced in the nitration of benzene and the completeness of nitration were demonstrated in two ways. First the nitrobenzene produced in the kinetic run (the concentration of which was calculated from the initial concentration of benzene) was shown to have the *same extinction coefficients* as nitrobenzene (purified by chromatography through activated alumina) in the region 350–400 mμ. Second the constancy of the ratio of concentrations of product to reactant (Table I) demonstrated that if the same product was not always formed, at least the same ratio of products resulted.

With the other five substituted benzenes used as reactants, only the second criterion was used, since to test eq. 3 and 5, it was only necessary that a constant ratio of mononitrated products be formed.

Methoxybenzene produced an interesting problem. When the kinetics were measured in the usual way, marked autocatalysis appeared so that the data did not even approach first-order kinetics. However, the ratio of product to reactant was always constant indicating that the same ratio of products appeared and that the reaction went to completion despite the widely varying nature of the kinetics. When 0.1 g. of urea was added to each run, the kinetics were perfectly first order to 95–99% of completion and the ratio of spectroscopic absorption of product to reactant was the same as in runs without urea. The effect undoubtedly is that studied by Ingold, *et al.*,[4] and by Schramm and Westheimer,[5] who found that methoxybenzene was nitrosated rapidly in the presence of intermediate oxidation states of nitrogen and that the nitric acid rapidly oxidized the nitroso group to a nitro group. The intermediate oxidation states of nitrogen thus function as a catalyst for nitration.

The immediate objective of this work was to test eq. 3 and this has been done by first differentiating eq. 3 with respect to % H_2SO_4 to yield eq. 8. In Table III the test of eq. 8 is summarized. The kinetic data of Westheimer and Kharasch[6] and of Williams and Lowen[7] were employed as well as our own.

$$\mathrm{d}\log k/\mathrm{d}\ \%\ \mathrm{H_2SO_4} = -\mathrm{d}C_0/\mathrm{d}\ \%\ \mathrm{H_2SO_4} \qquad (8)$$

The fit of the data with eq. 8 from 40–62.5% H_2SO_4 is excellent providing that $pK = -2.80$ is chosen for the equilibrium, $NO_3^- + H^+ = HNO_3$, and that it is assumed that this equilibrium will follow eq. 1, although it is of a different charge type. We hope to confirm these two provisions with independent data at a later date. In any event they do not affect the fit from 50–62.5% H_2SO_4. From 65–85% H_2SO_4, d log k/d % H_2SO_4 is 35–50% too large and the deviation is independent of the substituted benzene.

These deviations cannot be explained by postulating increasing protonation of HNO_3 above 65% H_2SO_4 because this condition would cause the deviation to be in the opposite direction to that observed. Likewise protonation of the substituted benzene would also cause the deviations to be in the opposite direction to that observed. In addition, in the case of benzene, the data in Table I show that the solubility of benzene is constant from 54–69% H_2SO_4; thus no significant amount of benzene could be protonated. Also in the case of nitrobenzene, spectroscopic[8] and *i*-factor[9] evidence demonstrated that nitrobenzene was not significantly protonated in 80–88% sulfuric acid.

The deviations from eq. 3 or 8 thus seem to be due to failure of eq. 5. An optimistic consideration in regard to the usefulness of eq. 3 is that since NO_2^+ differs in such a pronounced manner in structure from the R^+ species used to evaluate C_0, the deviations listed in Table III may represent almost limiting deviations.

One reason for the deviation from eq. 8 in the 65–80% H_2SO_4 region is as follows. The activity coefficients for a variety of oxygen-containing compounds undergo sharp changes in this region as evidenced by the sharply changing solubilities which are not due to protonation.[10] When activity coefficients are sharply changing, the greatest strain is put on the validity of eq. 5. This is in contrast to regions of acid concentration in which activity coefficients are constant and both sides of eq. 5 reduce to zero.

---

(4) E. L. Blackall, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 28 (1952); C. A. Bunton, E. D. Hughes, C. K. Ingold, D. I. Jacobs, M. H. Jones, G. J. Minkoff and R. I. Reed, *ibid.*, 2628 (1950).

(5) R. M. Schramm and F. H. Westheimer, THIS JOURNAL, **70**, 1782 (1948).

(6) F. H. Westheimer and M. Kharasch, *ibid.*, **68**, 1871 (1946).

(7) G. Williams and A. M. Lowen, *J. Chem. Soc.*, 3315 (1950).

(8) J. C. D. Brand, *ibid.*, 997 (1950).

(9) H. P. Treffers and L. P. Hammett, THIS JOURNAL, **59**, 1708 (1937).

(10) L. P. Hammett and R. P. Chapman, *ibid.*, **56**, 1282 (1934).

TABLE III

VARIATION OF RATES OF AROMATIC NITRATION WITH CONCENTRATION OF SULFURIC ACID (TEST OF EQ. 8)

% H_2SO_4	$\frac{-dC_0}{d\ \%\ H_2SO_4}$	d log k/d % H_2SO_4 for C_6H_5R[a] R = OCH$_3$	H	F	Cl	Br	CN	N(me)$_3^+$	NO$_2$	N(me)$_3^+$
40	0.16	0.16								
42.5	.17	.17								
45	.18	.18								
47.5	.19	.19								
50	.20	.20	0.21							
52.5	.21	.21	.22							
55	.23	.24	.24	0.23						
57.5	.24	.25	.24	.23	0.23	0.24				
60	.26	.28	.26	.26	.27	.26				
62.5	.26	.31	.29	.29	.32	.31				
65	.26		.36	.36	.35	.36				
67.5	.26		.36	.36	.35	.36				
70	.26				.35	.36				
72.5	.26				.35	.36				
75	.26									0.40
77.5	.26									.40
80	.26						0.39		0.39	.40
82.5	.26						.39	0.37	.39	.40
85	.26						.39	.37	.39	
87.5	.26							.37	.39	

[a] These derivatives were estimated from smooth curves of plots of log k against % H_2SO_4. No correction was made for any change in acidity due to addition of the nitric acid. The data for the last three compounds (NO_2 and the two quaternary amines) were taken from the paper of Williams and Lowen (ref. 7 in text). These authors also measured alcohol–carbonium ion equilibria for 4,4′,4″-trinitro, 4,4′,4″-tris-(trimethylammonium)- and 4,4′-bis-(trimethylammonium)-triphenylmethanol in the 78–95% H_2SO_4 region. Calculations based on their data resulted in the same values for $-dC_0/d$ % H_2SO_4 as from our data. [b] This compound also contained a 4-methyl substituent.

Finally, the values of d log k/d % H_2SO_4 were not simply related to any other acidity function. The rates of change of H_0, log a_{H_2O} and log $c_{H_3O^+}$ with % H_2SO_4 are all less than half the corresponding value for C_0, so that the deviations of the data from these acidity functions were very large.

We consider that the work reported herein has further supported eq. 6 as the general mechanism for aromatic nitration. Although we have emphasized the deviations of the data from eq. 3 or 8 and other authors have not,[3,7] in the 78–88% H_2SO_4 region previously studied,[7] both the earlier data and our data lead to the same deviations (*cf.* footnote *a* in Table III).

Experimental

A typical run with fluorobenzene will be described. All optical densities were measured at 25 ± 0.1° in a Beckman model DU spectrophotometer. The temperature control was achieved by means of thermospacers through which water was circulated.

Two 1 cm. silica cells were filled with the desired sulfuric acid. The optical densities were measured at 260 and 340 mμ. These readings were generally very close to zero and constituted a blank correction. The sample cell was filled with a sulfuric acid solution of fluorobenzene which had been prepared by dissolving one drop of acetic acid containing a small amount of fluorobenzene into about 28 ml. of the desired acid. The optical density was measured at the same two wave lengths. One ml. of 70% nitric acid was then dissolved in 25.0 ml. of this sulfuric acid solution of fluorobenzene. The optical density was measured nearly continuously in short runs and periodically in long runs. This addition of nitric acid caused the temperature to rise about 1°. In long runs this made little difference since temperature equilibrium was achieved in about four minutes. In short runs, either a small correction was made or the reagents were mixed at 24°.

All runs with chlorobenzene, bromobenzene and benzonitrile were performed in the above manner except for the wave lengths used for measurement. With methoxybenzene, about 0.1 g. of urea was added to the sulfuric acid before any spectroscopic measurements were made. With benzene, the sulfuric acid was saturated with benzene and the clear solution removed by a pipet. Thus the initial optical densities in the benzene runs are an approximate measure of the solubility of benzene in this medium. No precautions were used to insure complete saturation so that these solubilities are not exact.

Particularly with fluorobenzene, the final readings were not completely constant so that some discretion was necessary in choosing the value for a final reading. As a guide in this choice, the value at 7 half-lives was considered to be a maximum value for the final reading. The uncertainty was small and the lack of reproducibility precluded handling it in any more exact manner.

UNIVERSITY PARK, PA.