compared its reactivity to that of phenylacetylene.

Under similar conditions mesitylacetylene adds only one molecule of bromine to form 1,2-dibromo-1-mesitylethylene whereas phenylacetylene adds two molecules of bromine to form the expected tetrabromide. Attempts to add more bromine to the above dibromide resulted only in nuclear bromination. Similarly, mesitylacetylene did not add two molecules of methanol to yield the expected acetal of acetomesitylene under conditions where phenylacetylene readily did so. Evidence for the addition of one molecule of methanol to form the enol ether of acetomesitylene was obtained, although this compound was not isolated in a pure state. It was possible to hydrate mesitylacetylene to acetomesitylene. However, it is necessary to add only one molecule of water to the triple bond to effect this transformation. Thus, we have obtained evidence which provides support for Kadesch's theoretical considerations[3] and extends them to functions other than the carbonyl group.

Experimental

Mesitylacetylene.—1-Chloro-1-mesitylethylene, b. p. 99–105° at 1 mm., prepared in 65% yield from acetomesitylene, was converted in 76% yield into mesitylacetylene, b. p. 63–68° at 2 mm., n^{25}_{D} 1.5422, in agreement with the recent literature.[5,7] The known mercury derivative,[8] m. p. 238–240° uncor., was obtained.

Reactions of Mesitylacetylene and Phenylacetylene.—To an ice-cold solution of 10 g. of mesitylacetylene in 15 cc. of chloroform was added slowly a solution of pure bromine in chloroform until the bromine color persisted. The chloroform was then removed and the residue distilled and redistilled to yield 2 g. (44%) of 1,2-dibromo-1-mesitylethylene, b. p. 132–134° at 4–5 mm. Attempts to add bromine to this product were unsuccessful. At higher temperatures bromine was taken up but copious evolution of hydrogen bromide occurred.

Anal. Calcd. for $C_{11}H_{12}Br_2$: C, 43.5; H, 4.0; Br, 52.6. Found[9]: C, 44.8; H, 3.9; Br, 51.8.

In a comparable experiment phenylacetylene[10] was converted into 1,1,2,2-tetrabromophenylethane, m. p. 74–74.5°, in 92% yield. This compound had been described as a liquid.[11] For analysis the compound was recrystallized from alcohol.

Anal. Calcd. for $C_8H_6Br_4$: C, 22.8; H, 1.4; Br, 75.8. Found[9]: C, 22.8; H, 1.7; Br, 75.7.

Under anhydrous conditions a solution of 7.2 g. of mesitylacetylene, 5.2 cc. of absolute methanol, 0.5 g. of red mercuric oxide, and 0.2 cc. of boron trifluoride etherate was allowed to stand at room temperature for two days.[12] After suitable procedure 5 g. of a colorless liquid, b. p. 75–77° at 2 mm. was obtained. This compound was not pure, but its infrared spectrum indicated the presence of the ether linkage and carbon–carbon unsaturation. The low methoxyl value obtained on analysis (8.5%[9] as compared with a theoretical value of 17.6% for the methyl enol ether of acetomesitylene) makes it unlikely that any acetal was present. An attempt to add methanol in the presence of sodium methylate was unsuccessful, starting material being recovered (81%). Under similar conditions, phenylacetylene yielded 67% of acetophenone dimethylacetal,[13] b. p. 74–76° at 8 mm.

The hydration of mesitylacetylene to acetomesitylene was accomplished in 54% yield essentially according to the hydration method used for benzylphenylacetylene.[14] The acetomesitylene was characterized as its dinitro derivative, m. p. 137–139°, mixed m. p. with authentic sample[15] not depressed.

Summary

Mesitylacetylene adds one molecule of bromine. The dibromide thus formed does not add bromine. The theoretical implications of these findings are discussed.

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[7] R. C. Fuson and J. S. Meek, *J. Org. Chem.*, **10**, 551 (1945).

[8] T. H. Vaughn, THIS JOURNAL, **55**, 3453 (1933).

[9] Microanalysis by H. S. Clark Analytical Laboratory, Evanston, Ill.

[10] Prepared according to J. C. Hessler, *Org. Syn.* Coll. Vol. I, p. 438 (1943).

[11] L. P. Kinnicutt and G. M. Palmer, *Am. Chem. J.*, **5**, 387 (1883).

[12] Compare G. F. Hennion, D. B. Killian, T. H. Vaughn and J. A. Nieuwland, THIS JOURNAL, **56**, 1130 (1934).

[13] M. T. Bogert and P. P. Herrera, *ibid.*, **45**, 243 (1923).

[14] J. R. Johnson, T. L. Jacobs and A. M. Schwartz, *ibid.*, **60**, 1885 (1938).

[15] R. C. Fuson and J. T. Walker, *ibid.*, **52**, 3273 (1930).

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[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

Kinetics of the Iodination of Aniline

BY ERNST BERLINER

From a study of the kinetics of the iodination of phenol in water Painter and Soper concluded that the reaction takes place either between phenol and hypoiodous acid, or between the phenoxide ion and the positive iodine ion (I^+).[1] Since the aromatic rings of both phenol and the phenoxide ion are very reactive toward electrophilic reagents, a distinction between these two reaction schemes could not be made on chemical grounds, but the authors preferred the latter of the two possibilities. If the iodination of aniline is similar to the iodination of phenol, a more clear-cut distinction between the positive iodine ion and hypoiodous acid as the iodinating species might be possible, because the two aromatic compounds, aniline and the anilinium ion, behave very differently in electrophilic aromatic substitution reactions. Wistar and Bartlett have on the same basis shown that the diazo coupling reaction of aromatic amines takes place between free aniline and the diazonium cation, whereas the kinetic data for the diazo coupling of phenols did not make such

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[1] Painter and Soper, *J. Chem. Soc.*, 342 (1947); Soper and Smith, *ibid.*, 2757 (1927).

a distinction possible.[2,3] It was thus expected that the iodination of aniline would present a more favorable case than that of phenols for the study of the mechanism of iodination. The following reports a study of the kinetics of the iodination of aniline in water in the presence of different buffers and different concentrations of iodide ion. It was hoped that it might not only be possible to determine the nature of the iodinating species, but also to gain some clearer insight into the details of the process of aromatic substitution.

Experimental

Materials.—The iodine, the buffer salts, potassium iodide and sodium chloride were best commercial Reagent Grade chemicals and were used without purification. The acetic acid was a sample purified by the method of Orton and Bradfield.[4] Two samples of aniline were tested. One was prepared by hydrolysis of acetanilide, and the other was Merck Reagent Grade aniline. Both samples were distilled twice from zinc dust. Since they gave identical results in preliminary kinetic experiments, the latter sample was used throughout; its boiling point was 183.2° at 756 mm. and 62° at 6 mm. The aniline, which was stored in an amber bottle, remained colorless throughout the time of the experiments. All reagents were weighed to four places.

Kinetic Runs.—Stock solutions of aniline, the buffers and sodium chloride were prepared separately at such concentrations that a certain number of milliliters of each diluted to 100 ml. gave a solution of the desired concentration. The iodine solution (0.02 *M*) was always made up together with the potassium iodide (1.2 *M*) in a 100 ml. volumetric flask; ten milliliters of this solution was used in the kinetic experiments.

Solutions of all reagents were pipetted into a 250 ml. Erlenmeyer flask, the solution was diluted to 90 ml. and brought to temperature in a thermostat (25 ± 0.05°). Ten milliliters of the iodine–iodide solution, also at the thermostat temperature, was pipetted into the Erlenmeyer flask with vigorous swirling, and a 10-ml. sample was immediately withdrawn. This operation never required more than 30 seconds. The sample was run into 20 ml. of 1 *N* sulfuric acid, and this time was taken as zero time. The iodine was titrated with a 0.02 *M* thiosulfate solution from a 5-ml. buret graduated in hundredths, using starch as an indicator. The thiosulfate solution was prepared fresh every day by diluting a 0.1 *M* stock solution. Eight 10-ml. samples were then withdrawn at suitable time intervals. The rate constants were calculated from the integrated form of the second-order rate equation

$$k = \frac{2.303}{t(a-b)} \log \frac{b\,(a-x)}{a\,(b-x)}$$

where a and b refer to the initial aniline and iodine concentrations, and x is the amount of iodoaniline formed. An average of all k's was taken. At least two determinations were made for each set of concentrations. They usually agreed within 1–2%. Another determination was made when the discrepancy was greater. The *p*H of the buffers was determined with a Leeds and Northrup *p*H meter using acid potassium phthalate as a standard. The buffers to be measured were always made up in a solution whose ionic strength was brought to 0.3 by the addition of sodium chloride.

Isolation.—A run (phosphate buffers 0.04 *M*, iodine 0.004 *M*, aniline 0.004, *M*, KI 0.12 *M*, μ = 0.3) was carried out on a one-liter scale. After the iodine color had disappeared almost completely, the solution was treated with an excess of sodium bisulfite and a few pellets of sodium hydroxide. The solution was extracted with ether exhaustively; the ether extract was dried and the ether evaporated. The residue was dissolved in 5 ml. of benzene and 2 ml. of ligroin, and 2.5 ml. of acetic anhydride was added. The mixture was warmed for a few minutes on the steam-bath and then cooled. The crystalline material which separated was filtered and weighed 0.770 g. (73.7%). It softened around 150° and melted unsharply at 178.7–182.2°. The melting points of *o*-iodoacetanilide, *m*-iodoacetanilide, and 2,4-diiodoacetanilide are all below the one found (109–110°; 119.5°; 141° (171°)). *p*-Iodoacetanilide melts at 183–184°, and the recovered material therefore consisted chiefly of the latter. The material was recrystallized from alcohol and afforded 0.597 g. of pure *p*-iodoacetanilide, m. p. 182.1–183.7°; and 0.071 g., m. p. 182.6–184°, was obtained from the mother liquor. The total yield of pure product is 64%. A mixed melting point with an authentic sample of *p*-iodoacetanilide showed no depression. All of the mother liquors contained material which softened at 150° and did not melt below 180°. For this reason, and because the acetylation may not have been quantitative, the recorded yield constitutes a minimum.

Results

The reaction between iodine and aniline in water, at the concentrations studied, follows a second-order equation and is first-order with respect to aniline and first-order with respect to titratable iodine. In Table I are recorded the data for two typical runs; the data in Table II show that the rate constants do not change within the indicated variations of the initial concentrations of aniline and iodine.

TABLE I

THE IODINATION OF ANILINE AT 25° IN WATER

Time, min.	0.02 *M* thiosulfate, ml.	k(liters mole^{-1} min.$^{-1}$)
Aniline 0.003957 *M*, KI 0.12 *M*, KH_2PO_4 0.04 *M*, Na_2HPO_4 0.01 *M*, NaCl 0.11 *M*, μ = 0.3		
0	2.000	
52	1.834	(0.430)
108	1.681	.424
164	1.546	.423
240	1.385	.423
337	1.210	.424
404	1.109	.423
470	1.022	.421
520	0.958	.423
	Av.	.423
Aniline 0.004001 *M*, KI 0.12 *M*, KH_2PO_4 0.004 *M*, Na_2HPO_4 0.032 *M*, NaCl 0.08 *M*, μ = 0.3		
0	2.002	
22	1.830	1.044
45	1.669	1.056
64	1.554	1.052
87	1.428	1.052
112	1.306	1.055
137	1.195	1.062
167	1.082	1.061
197	0.982	1.062
	Av.	1.055

Influence of Buffers.—The iodination reactions were studied in eleven different phosphate buffers corresponding to a change of *p*H from 5.59 to 7.59 with a maximum ratio of buffer

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(2) Wistar and Bartlett, THIS JOURNAL, **63**, 413 (1941).

(3) Conant and Peterson, *ibid.*, **52**, 1220 (1930).

(4) Orton and Bradfield, *J. Chem. Soc.*, 983 (1927).

TABLE II

THE IODINATION OF ANILINE WITH DIFFERENT INITIAL CONCENTRATIONS OF REACTANTS AT 25°

KI 0.12 *M*, KH_2PO_4 and Na_2HPO_4 0.02 *M*, NaCl 0.1 *M*

Molarity of aniline $\times 10^3$	Molarity of iodine $\times 10^3$	*k*(liters moles^{-1} min.$^{-1}$)
8.018	1.000	0.720
6.014	1.002	.716
4.009	1.002	.702
4.009	1.511	.704
8.018	1.973	.718
6.014	1.981	.704
4.009	2.002	.709
3.007	2.007	.713
2.004	2.012	.707
4.009	3.985	.711
		Av. 0.710

constituents of 10:1, and in five different acetate buffers of a *p*H range of 4.57 to 5.53. The total *p*H range over which the reaction was studied therefore corresponded to a change of hydrogen ion concentration by a factor of a thousand.

The iodination reaction shows general catalysis by the buffer constituents, which cannot be due to a salt effect, because the ionic strength was kept constant throughout all runs by the addition of sodium chloride ($\mu = 0.3$). At any one *p*H an increase of the concentration of the buffers was found to increase the rate. This is also observed in the iodination of phenols in water.[1] In phosphate buffers the change in rate is caused almost exclusively by a change in the concentration of the secondary phosphate ion (Na_2HPO_4) and is almost independent of the concentration of the buffer acid (KH_2PO_4). The reaction is thus base catalyzed. The dependence of the rate on the concentration of the buffer base is shown in Table III. As can be seen from this table, the base catalyzed reaction is independent of the hydrogen ion concentration. At very high concentrations of buffer acid and at low *p*H's a very slight additional catalysis by the primary phosphate ion, $H_2PO_4^-$, is observed. This is not considered to be due to an acid catalysis, but since the ion $H_2PO_4^-$ is also a base, though a weak one, is attributed to additional base catalysis by $H_2PO_4^-$. Since the catalytic power of $H_2PO_4^-$ is much weaker than that of $HPO_4^=$, catalysis by the former is only noticeable at high concentrations of this ion, *i.e.*, at low *p*H. The catalytic constants were calculated from the equation

$$k_{\text{obs.}} = k_0 + [\text{HA}]\left\{k_{\text{A}}\frac{[\text{A}]}{[\text{HA}]} + k_{\text{HA}}\right\}$$

where [A] and [HA] are the concentrations of secondary and primary phosphate respectively, and k_{A} and k_{HA} are the corresponding catalytic constants. The observed rate constants were plotted against the primary phosphate ion concentration at different buffer concentrations. For any one *p*H a straight line is obtained whose slope is equal to $k_{\text{A}}[\text{A}]/[\text{HA}] + k_{\text{HA}}$ (see Fig. 1).

TABLE III

THE EFFECT OF THE BUFFER CONSTITUENTS ON THE RATE OF IODINATION OF ANILINE AT 25°

KI 0.12 *M*, $\mu = 0.3$

Molarity of KH_2PO_4	Molarity of Na_2HPO_4	*k* obs. (liters mole^{-1} min.$^{-1}$)
0.1	0.02	0.736
.08	.02	.723
.03	.02	.709
.02	.02	.706
.005	.02	.704
.0025	.02	.706
.002	.02	.706
.045	.03	1.007
.03	.03	1.005
.02	.03	1.002
.003	.03	1.001
.1	.01	0.446
.05	.01	.423
.04	.01	.421
.015	.01	.418
.01	.01	.419
.0025	.01	.415
.001	.01	.413
.01	.04	1.292
.01	.015	0.556
.01	.01	.419
.03	.045	1.457
.03	.03	1.005
.03	.02	0.709

A plot of all of the slopes against the salt ratio [A]/[HA] gives a new straight line whose slope is equal to k_{A}. The catalytic constant for the $HPO_4^=$ ion was thus found to be 29.3. By plotting the lower part of this line separately, k_{HA} (the intercept) is found to have a value of about 0.3. The secondary phosphate is then about 100 times stronger as a basic catalyst than primary phosphate. Secondary phosphate ion was also found to be a stronger basic catalyst than primary phosphate in the iodination of tyrosine.[5] A similar basic catalysis was observed with the acetate ion, but in the *p*H range studied a significant amount of aniline is present as the anilinium ion, so that the total rate also depends on the *p*H and decreases rapidly as the *p*H increases. The catalytic constant for the acetate ion is about 2.4; it is thus intermediate between primary and secondary phosphate, as it should be if the catalyzed iodination follows a Brönsted catalysis law.

The Uncatalyzed Reaction.—The purpose of measuring the reaction rates at different hydrogen ion concentrations was to determine the dependence of the rate on the *p*H. Since at any one *p*H the observed rate constant depends linearly on the concentration of the buffer constituents, the observed rate constant must be made up of two terms, one involving the catalyzed reaction and one for the uncatalyzed reaction. In order to find the value of the rate

(5) Li, *J. Chem. Soc.*, **66**, 228 (1944).

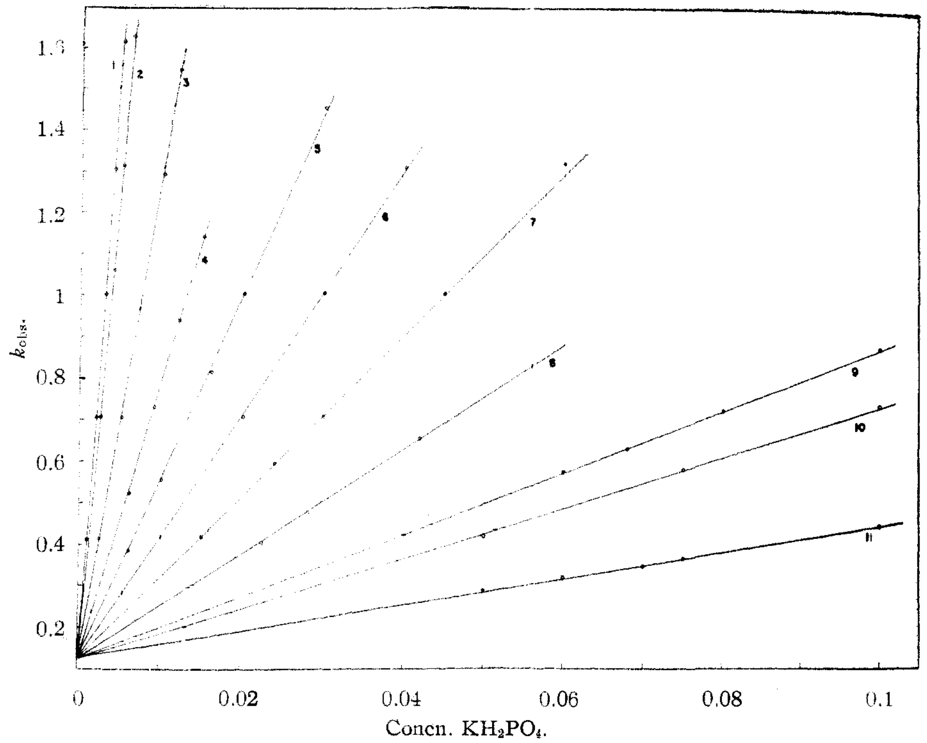

Fig. 1.—The influence of buffers on the iodination of aniline. The *p*H's to which the lines refer are 1–11: 7.59, 7.47, 7.24, 7, 6.71, 6.55, 6.41, 6.18, 6.02, 5.92, 5.59.

constant, k_0, for the uncatalyzed reaction, the observed rate constants for each constant buffer ratio were plotted against the concentration of the buffer acid (KH_2PO_4), and the lines obtained were extrapolated graphically to zero buffer concentration. The intercept for each line is equal to k_0 at that particular *p*H. The results of some typical runs at different hydrogen ion concentrations are recorded in Table IV. The results of the extrapolations are shown in Fig. 1, from which it can be seen that all lines converge in one point. The uncatalyzed reaction (or better, the water reaction) is therefore independent of the hydrogen ion concentration. The rate constants plotted in Fig. 1 were determined at *p*H's which correspond to a change in hydrogen ion concentration by a factor of one hundred. Over this *p*H range the rate constant for the uncatalyzed reaction, k_0, is equal to 0.123 with a mean deviation of 0.002. In acetate buffers of *p*H 5.53 and 5.44 the extrapolated values for k_0 are equal to 0.120 and 0.122, but at lower *p*H the rate falls off and is 0.059 at *p*H 4.57, because at higher hydrogen ion concentrations the amount of free aniline is less. Taking 3.8×10^{-10} as the dissociation constant of aniline, and neglecting as a first approximation the effect of the ionic strength on the dissociation constant, 10% of the aniline is present as anilinium ion at *p*H 5.53, and 50% at *p*H 4.57. The decrease of rate in acetate buffers is therefore not due to an intrinsic catalysis by acetic acid, but is due to the decrease in the amount of free aniline. A plot of the rate constants of the uncatalyzed reaction, obtained by extrapolation, against the hydrogen ion concentration is shown in Fig. 2. The curve, which increases up to a *p*H of about 5.4 and then remains constant, is similar to that describing the de-

TABLE IV

THE RATE OF IODINATION OF ANILINE AT VARYING BUFFER CONCENTRATIONS KI 0.12 *M*

$\mu = 0.3$

*p*H	Concn. KH_2PO_4	Concn. Na_2HPO_4	$k_{obs.}$	$k_{calcd.}$
6.55	0.04	0.04	1.312	1.307
	.03	.03[a]	1.005	1.011
	.02	.02[b]	0.706	0.715
	.01	.01	.419	0.419
			k_0[c] .123	
6.41	.06	.04	1.321	1.313
	.045	.03	1.007	1.015
	.03	.02	0.709	0.718
	.024	.016	.594	.599
	.015	.01	.419	.420
			k_0[c] .125	
5.59	.1	.01	.446	.446
	.075	.0075	.366	.365
	.07	.007	.348	.349
	.06	.006	.319	.317
	.05	.005	.288	.285
			k_0[c] .126	

[a] At an ionic strength of 0.5 $k_{obs.}$ is 0.955. [b] At an ionic strength of 0.5 $k_{obs.}$ is 0.68. [c] Extrapolated value.

pendence of the rate of diazo coupling of amines on the hydrogen ion concentration.[2]

The total rate constant for the iodination of aniline in phosphate buffers can be expressed by

$$k_{\text{obs.}} = k_0 + k_{\text{HA}}[\text{H}_2\text{PO}_4^-] + k_{\text{A}}[\text{HPO}_4^{=}] = 0.123 + 0.3[\text{H}_2\text{PO}_4^-] + 29.3[\text{HPO}_4^{=}]$$

and presumably by $k_{\text{obs.}} = k_0 + \Sigma k_{\text{B}}[\text{B}]$, where B is any basic catalyst. Rate constants calculated from the above equation are listed with the experimental values in Table IV.

The Effect of Iodide Ions.—The rate of the iodination reaction is strongly influenced by the iodide ion concentration, and the rate constants are inversely proportional to the square of the iodide ion concentration. This is shown in Table V, where the rate constants at different concentrations of iodide ion, but constant ionic strength ($\mu = 0.8$), are recorded. The product $k \times [\text{I}^-]^2$ is a constant over the range of iodide ion concentration studied. In that respect the iodination of aniline is similar to the iodination of phenol,[1] but different from the iodination of a number of pyrroles.[6]

Effect of Added Salts.—The reaction rates show a slight but noticeable dependence on the ionic strength, and decrease as the latter increases. A change of μ from 0.3 to 0.5 reduces the rate constant by about 4% (see footnotes in Table IV).

TABLE V .

THE EFFECT OF IODIDE ION CONCENTRATION ON THE RATE OF IODINATION OF ANILINE,

KH_2PO_4 and Na_2HPO_4 0.05 M, $\mu = 0.8$

Molar concn. of KI	k(liters mole^{-1} min.$^{-1}$)	$k \times (\text{KI})^2 \times 10^3$
0.1	2.073	20.7
.15	0.915	20.6
.2	.515	20.6
.25	.338	21.1
.3	.229	20.7
.35	.168	20.6
.4	.129	20.6
.5	.0827	20.7

Discussion

The fact which is most important for a consideration of the mechanism of the iodination of aniline is the observation that the rate of the reaction is independent of the hydrogen ion concentration and inversely proportional to the square of the iodide ion concentration. The total concentration of iodide was chosen so much larger than that of iodine that the formation of iodide ion during the reaction

$$\text{C}_6\text{H}_5\text{NH}_2 + \text{I}_2 \longrightarrow p\text{-IC}_6\text{H}_5\text{NH}_2 + \text{HI}$$

did not noticeably affect the rate constants, and the total iodide ion concentration can be considered constant during any one run. The liberated hydrogen iodide was taken care of by the buffer. The velocity of iodination is directly proportional to the initial iodine concentration and the concentration of aniline, *i. e.*, $-\text{d}x/\text{d}t = k_{\text{obs.}}$ (titratable iodine)(aniline). In a solution containing iodine and iodide ions the concentrations of the different species can be calculated from the equilibrium[7]

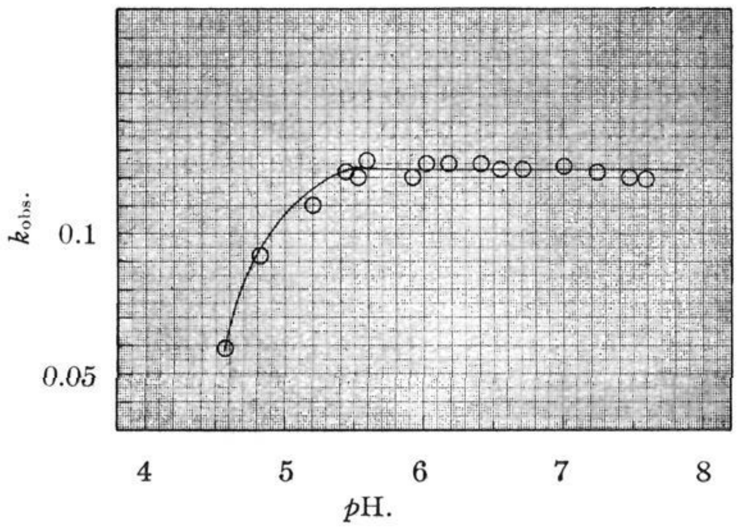

Fig. 2.—The influence of pH on the rate of the uncatalyzed reaction.

$$\text{I}_3^- \rightleftarrows \text{I}_2 + \text{I}^- \quad K_1 \qquad (1)$$

The concentration of iodide ion was always sixty times greater than that of iodine (0.12 M iodide ion, 0.002 M iodine) and in such a solution the free iodine is present to an extent of less than 1.5%.[8] Practically all of the iodine is present as I_3^-, and the rate equation becomes $-\text{d}x/\text{d}t = k_{\text{obs.}}(\text{I}_3^-)\cdot$(aniline).[1] The following equilibria have to be considered, in addition to equilibrium (1), in order to determine the nature of the iodinating species.[1]

$$\text{I}_2 + \text{H}_2\text{O} \rightleftarrows \text{HOI} + \text{H}^+ + \text{I}^- \quad K_2 \qquad (2)$$

$$\text{HOI} \rightleftarrows \text{I}^+ + \text{OH}^- \quad K_3 \qquad (3)$$

$$\text{HOI} \rightleftarrows \text{IO}^- + \text{H}^+ \quad K_4 \qquad (4)$$

$$\text{I}_2 \rightleftarrows \text{I}^+ + \text{I}^- \quad K_5 \qquad (5)$$

$$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}^+ \rightleftarrows \text{C}_6\text{H}_5\text{NH}_3^+ \quad K_6 \qquad (6)$$

Each of the iodine containing species, I_2, I_3^-, I^-, HOI, OI^-, I^+, is a potential iodinating agent. Iodide and triiodide ion can be ruled out because the rate decreases rapidly with the iodide ion concentration; they are also unlikely on chemical grounds. If iodine is the iodinating species, the rate of the reaction, from equilibrium (1), is $-\text{d}x/\text{d}t = k_{\text{obs.}}(\text{I}_3^-)(\text{PhNH}_2) = (k_1K_1/\text{I}^-)(\text{I}_3^-)(\text{PhNH}_2)$ and $k_{\text{obs.}}$ should be equal to k_1K_1/I^-. If hypoiodous acid is the iodinating agent, the observed rate constant should be equal to $k_2K_1K_2/(\text{H}^+)(\text{I}^-)^2$. The dependence of the rate constants on the hydrogen and iodide ion concentrations for these two cases is not the one found experimentally.[9] Iodine and hypoiodous acid must therefore be

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(6) Doak and Corwin, *J. Chem. Soc.*, **71**, 159 (1949).

(7) K_1 is 1.4×10^{-3}, Jones and Kaplan, THIS JOURNAL, **50**, 1845 (1928).

(8) Moelwyn-Hughes and Legard, *J. Chem. Soc.*, 424 (1933).

(9) A more exact expression for $k_{\text{obs.}}$ if iodine is the iodinating agent, is $k_{\text{obs.}} = k_1K_1/(K_1 + \text{I}^-)$, but since I^- is very much greater than K_1, the latter can be neglected in the denominator, and the expression takes the form used above. The same simplification is adopted for the other cases (see references 6 and 8).

ruled out as the iodinating agents for free aniline. The ion OI^- requires an inverse square relationship of the hydrogen ion concentration and is also ruled out. If the positive iodine is the iodinating agent, the observed rate constant should be equal to $k_3K_1K_2K_3/K_w(I^-)^2$ (or $k_5K_1K_5)/(I^-)^2$) and should therefore be independent of the hydrogen ion concentration and inversely proportional to the square of the iodide ion concentration, as found.

The kinetics of the iodination of aniline, at the concentrations studied, are therefore not incompatible with a mechanism in which the positive iodine is the iodinating agent of free aniline, but it is not compatible with a mechanism involving iodine or hypoiodous acid. The rate of the iodination can therefore be expressed as

$$-dx/dt = k_0[I^+][C_6H_5NH_2] + k'[B][I^+][C_6H_5NH_2]$$

However, the same kinetics are also in agreement with a reaction between hypoiodous acid and the anilinium ion ($k_{obs.} = k_6K_6K_2K_1/(I^-)^2$), and the two reactions are kinetically indistinguishable.

A reaction between hypoiodous acid and the anilinium ion is not only very unlikely from all that is known about aromatic substitution, but the anilinium ion is a strong *meta* director, whereas a minimum yield of 64% of *p*-iodoaniline (as *p*-iodoacetanilide) was isolated from the reaction mixture. In a large scale preparative procedure a 75–84% yield of *p*-iodoaniline is obtained by iodination of aniline in aqueous sodium bicarbonate solution.[10] The alternative involving the anilinium ion can therefore be excluded on chemical grounds. Furthermore, at the *p*H at which the concentration of anilinium ion becomes appreciable the rate falls off and would presumably reach zero when all free aniline is converted to the anilinium ion.

That I^+ should be the iodinating agent is gratifying from the point of view of modern theories regarding aromatic substitution for which an electrophilic substituting agent has always been postulated and in a few cases demonstrated.[11] It does not mean, and is indeed unlikely, that the results can be generalized to include Br^+ or Cl^+ (in the absence of a catalyst) or that I^+ will always be the iodinating agent. Free iodine apparently iodinates pyrroles, although not exclusively.[5] Mixtures of iodine and hypoiodous acid have been assumed to be responsible for the iodination of the nucleus of tyrosine and histidine, but the catalyzed and uncatalyzed reactions have not been separated.[12] More reactive aromatic compounds will probably require less drastic iodinating agents than I^+. Entirely different situations must be anticipated in non-aqueous solutions. The positive iodine is not an intrinsically unlikely iodinating agent when it is recalled that hypoiodous acid is a stronger base than it is an acid ($K_4 = 4.5 \times 10^{-13}$; $K_3 = 3.2 \times 10^{-10}$) and that the dissociation constant of iodine (into the positive and negative ion) K_5 is 9.6×10^{-9}.[13] The initial concentration of I^+ in the present experiments, neglecting again the effect of ionic strength, is 1.9×10^{-12}, and the specific rate constant for the uncatalyzed reaction of I^+ with aniline is 1.3×10^8. Since the concentration of iodine is of the order of 10^{-5}, I^+ is about 10^7 times more reactive than iodine. The concentration of I^+ is not appreciably smaller than that of HOI; the latter is 6×10^{-10} *M* at a *p*H of 7 and 6×10^{-12} *M* at a *p*H of 5. I^+ must therefore be an appreciably more effective iodinating agent than hypoiodous acid. The concentrations of Br^+ or Cl^+ in an aqueous solution of bromine or chlorine would be smaller by many powers of ten.[14] The I^+ probably attaches itself to water and is never "free"; but it cannot be attached to iodine (I_3^+) at the moment of substitution, because this would require a different rate expression. That the reaction should show general base catalysis is also in agreement with present views, and a similar catalysis was shown in the nitration of aromatic compounds in sulfuric acid where the bisulfate ion accelerates the rate.[15] The bromination of hydrocarbons in acetic acid is accelerated by sodium acetate.[16] Since the transition state in electrophilic aromatic substitution has the properties of an acid, a base must always be present to complete the reaction. The role of the phosphate or acetate ions is therefore concerned with the removal of a proton from the transition state.

In the absence of the base the reaction is slower, because the place of the base has to be taken by the much weaker base, water. The uncatalyzed reaction is therefore visualized as one in which the water plays the part of the base.

The assignment of a specific function to the base is based on the assumption that the breaking off of the proton is part of the rate determining step. However, Melander, in a recent note,[17] has shown that in the nitration of benzene and toluene tritium is replaced as rapidly as hydrogen, from which he concluded that the splitting off of the proton in aromatic substitution is not part of the rate determining step, but that it is a rapid process which occurs after the transition state is passed. This view is clearly in conflict with the interpretation of Bennett, *et al.*[15]

If the view of Melander is taken, and if it is *generally* true that the proton departs in a fast fol-

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(10) Brewster, "Organic Syntheses," Coll. Vol. II, 1943.

(11) See for instance, Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 256 ff., also ref. 15.

(12) Li, THIS JOURNAL, **64**, 1147 (1942); **66**, 225 (1944); **70**, 1716 (1948)

(13) Murray, *J. Chem. Soc.*, **127**, 882 (1925); Skrabal, *Ber.*, **75**, 1570 (1942). The hydrolysis constant for iodine K_2 is 3×10^{-13}. Bray and Connolly, THIS JOURNAL, **33**, 485 (1911).

(14) Bartlett and Tarbell, *ibid.*, **58**, 466 (1936). The dissociation constant for bromine was estimated by these authors to be less than 7×10^{-16}.

(15) Bennett, Brand, James, Saunders and Williams, *J. Chem. Soc.*, 474 (1947).

(16) Berliner and Berliner, THIS JOURNAL, **71**, 1195 (1949).

(17) Melander, *Acta Chem. Scand.*, **3**, 95 (1949).

low-up reaction, the base cannot have the role assigned to it in the iodination of aniline. What the function of the base is cannot be decided on the basis of the kinetic data alone, but another interpretation of the results is possible. Because of the acid-base equilibria of the buffer constituents, the kinetic data are also in agreement with an acid catalyzed reaction of hypoiodous acid and aniline with a possible transition state as shown in Fig. 3. The rate expression

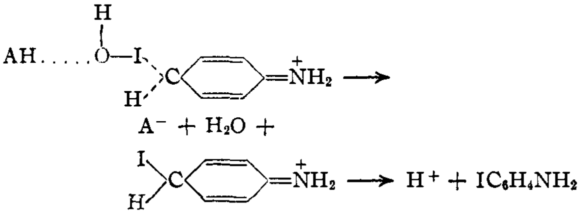

Fig. 3.

would then be $dx/dt = k_0[H^+][HOI][C_6H_5NH_2] + k'[HA][HOI][C_6H_5NH_2]$, and the role of the acid might consist in weakening, through hydrogen bonding, the oxygen–iodine bond of hypoiodous acid. The "water reaction" of I^+ and aniline would be identical with a reaction of hypoiodous acid and aniline catalyzed by hydrogen ions ($k_{\text{obs.}} = k_7K_1K_2/[I^-]^2$), and the base catalyzed reaction of I^+ would become the general acid catalyzed reaction of hypoiodous acid. The complex of hypoiodous acid and an acid can be described as a "solvated I^+," so that the iodinating agent can still be the I^+ ion, although the role of the base is different.[18]

A distinction between the two possibilities cannot be made until more is known about the transition state in aromatic substitution.

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Summary

The kinetics of the iodination of aniline in water were studied in the presence of iodide ions and at different hydrogen ion concentrations. The reaction shows general base catalysis, and the kinetics are in agreement with a mechanism involving the positive iodine ion as the iodinating agent of free aniline.

An alternate mechanism involves an acid catalyzed reaction of aniline and hypoiodous acid.

[18] I am indebted to the Referees for calling my attention to the Note of Melander and to one of them for suggesting the alternate interpretation of the results.

BRYN MAWR, PA. RECEIVED JANUARY 27, 1950

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Heat Capacities, Dielectric Constants and Molecular Rotational Freedom in Solid Trichloroethanes and Disubstituted Propanes[1]

BY ROBERT W. CROWE AND CHARLES P. SMYTH

A number of substances whose molecular shapes are not far from spherical have been found to show polymorphism, the solids apparently possessing molecular rotational freedom for some distance below the melting points. Dielectric constant measurements have given evidence of this in 2-chloro-2-methylpropane,[2] 2-bromo-2-methylpropane,[2] 2,2-dichloropropane[3] and 1,1,1-trichloroethane[3] among others. It has been shown[4] that the molecular rotation in the solid leads to an abnormally high melting point. Although the liquid range of 1,1,2-trichloroethane, 151°, is somewhat larger than that of 1,1,1-trichloroethane, 107°, its rather high melting point, −36.0°, suggested that this substance also might possess some molecular rotational freedom in its crystal lattice. Simultaneous heat capacity and dielectric constant measurements or dielectric constant measurements alone were, therefore, made upon these substances and upon other compounds containing different groups attached to a central carbon atom. The measurements were carried out with an apparatus and method which have been previously described.[5]

Purification of Materials

1,1,1-Trichloroethane and 1,1,2-Trichloroethane.—Both compounds, obtained from the Eastman Kodak Company, were washed twice with 6 *N* sodium carbonate solution and with several portions of distilled water. They were then dried over anhydrous calcium chloride for twenty-four hours and fractionally distilled repeatedly at atmospheric pressure in a five-foot column. The physical constants of these compounds are

	This research			Literature		
	M. p., °C.	B. p., °C.	$n^{20}D$	M. p., °C.	B. p., °C.	$n^{20}D$
1,1,1-Trichloroethane	−33.0	74.0	1.4373	−32.7[3]	74.0[3]	1.4379[3]
1,1,2-Trichloroethane	−36.0	113.6		−36.7[6]	113.5[6]	

1,3-Dibromopropane.—Material from the Eastman Kodak Co. was washed several times

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[1] This research was supported by the Office of Naval Research. Reproduction, translation, publication, use and disposal in whole or in part by or for the United States Government is permitted.

[2] Baker and Smyth, THIS JOURNAL, **61**, 2798 (1939).

[3] Turkevich and Smyth, *ibid.*, **62**, 2468 (1940).

[4] Baker and Smyth, *ibid.*, **61**, 1695 (1939).

[5] Kushner, Crowe and Smyth, *ibid.*, **72**, 1091 (1950).

[6] "International Critical Tables."