

The iodination of acetophenone exhibits a general acid catalysis.

Direct evidence is offered to show that the pro-

ton removal is the rate determining step in the acid catalyzed enolization of ketones.

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Kinetics of the Iodination of Acetophenone in Sulfuric and Perchloric Acid Solutions

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The acidity function H_0 ² for sulfuric acid-water solutions (and for aqueous solutions of some other strong acids) combines in one functional representation all effects of continuing increase in acid concentration on the ionization equilibria of electrically neutral monoacid bases. These effects are presumably two—the result of increasing the acidity *per se*, and the result of changing the thermodynamic nature of the medium. There is also excellent correlation between the rates of some acid catalyzed reactions in increasingly acid solutions, and the acidity function for these solutions^{2,3} and consequently between the effects of increasing acid concentration on the rates of these acid catalyzed reactions, and on the ionization equilibria of electrically neutral monoacid bases. This is simply explained in terms of the transition state theory of reaction velocity if the equilibrium between reactants and activated complex, whose position determines the rate of the reaction, is or approximates an ionization equilibrium of the correct charge type.

On the other hand, the bromination of *m*-nitroacetophenone in moderately concentrated solutions of sulfuric acid in acetic acid-water mixtures shows no such correlation of rate with acidity function.⁴ This might be a property of the acetic acid medium or it might be a characteristic property of the enolization reaction. We have therefore studied the rate of iodination of acetophenone in sulfuric acid-water and perchloric acid-water solutions.

Experimental

Rate Measurements.—The colorimetric method used was that previously described.⁵

(1) Part of a thesis submitted by Lois Zucker in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

(2) Hammett and Deyrup, *THIS JOURNAL*, **54**, 272 (1932); Hammett and Paul, *ibid.*, **56**, 827 (1934).

(3) Hammett and Paul, *ibid.*, **56**, 830 (1934); Hammett, *Chem. Rev.*, **16**, 67 (1935).

(4) Paul and Hammett, *THIS JOURNAL*, **58**, 2182 (1936).

(5) Zucker and Hammett, *ibid.*, **61**, 2779 (1939).

The color of iodine in sulfuric acid solutions changes in hue from brown in the most dilute solutions to rose in 95% solution, and the effective extinction coefficient for the blue-violet light used slowly decreases. The change becomes perceptible with 46% sulfuric acid solution; for 46 and 51% solutions a pinker colorimetric standard is necessary to get a good match, and is supplied conveniently by an aqueous solution of methyl orange of the same concentration as that used for more dilute acid solutions, but buffered at pH 3.8 with 0.05 molar acetate buffer. The effective extinction coefficient of the iodine decreases by about 2% from 39.5 to 45.9% sulfuric acid, and by another 3% from 45.9 to 51% sulfuric acid. No hue which can be obtained from methyl orange at any reasonable acidity is sufficiently like that of iodine in 66% sulfuric acid solution with light of the spectral composition used to allow precise matching. The one experiment in 66% sulfuric acid was very crudely done by measuring the times at which the reacting solution matched, to the eye, various standard iodine solutions all in bottles of closely similar shape and color.

Both potassium iodate and sodium nitrite were satisfactory oxidizing agents for the more dilute acid solutions, up to and including 25% sulfuric acid. Potassium iodate could not be used in 39.5% sulfuric acid; iodine solutions made up from potassium iodide and excess potassium iodate increase steadily in depth of color for several minutes after mixing, although the iodine production should be practically instantaneous. If a large excess of potassium iodate is present, the color then decreases slowly over a period of days to weeks. In 70% sulfuric acid an iodine solution saturated with potassium iodate takes only a few days for complete decolorization. These two phenomena (production of more intense color, and decolorization) are instantaneous in 95% sulfuric acid with suitable relative concentrations of iodine and potassium iodate and are ascribed by Masson, *et al.*,⁶ to the formation of stabilized ions on the oxidative level of I⁺ (dark brown) and I⁺⁺⁺ (colorless), respectively. One or both of these ions seems to be kinetically active in 39.5% sulfuric acid. No difficulties were observed with sodium nitrite which was used exclusively for all the sulfuric acid solutions more concentrated than 25%. The innocuousness of this oxidizing agent could not be tested by comparing results obtained with it with those obtained with some other agent, because no other suitable oxidizing agent was found. Nor could rates in the presence of

(6) (a) Masson and Race, *J. Chem. Soc.*, 1718 (1937); (b) Masson and Hanby, *ibid.*, 1699 (1938); (c) Masson and Argument, *ibid.*, 1702 (1938); (d) Masson, *ibid.*, 1708 (1938).

nitrite be compared with rates without any oxidizing agent, because the rate of the reverse reaction between phenacyl iodide and iodide ion increases rapidly with acidity; iodination in 39.5% sulfuric acid will hardly proceed at all without an oxidizing agent. The concentration of sodium nitrite used was approximately that necessary to cause the initial oxidation of iodide to iodine, and to take care of all the iodide which might be formed during the reaction, assuming nitrite and iodide equivalent on a molar basis. Since 1 mole of nitrite will oxidize somewhat more than 1 mole of iodide, this procedure left some factor of safety.⁷ In 39.5% sulfuric acid, good agreement was obtained among the specific rates determined under these conditions over a 13-fold variation in acetophenone concentration, and a 700-fold variation in iodine concentration. The first effect of increasing the nitrite concentration was to cause some reversal of the reaction, probably due to replacement of iodide by nitrite in the phenacyl iodide. This reversal was only detected in the presence of two to three times the concentration of nitrite ordinarily used, and then only when over 30% of the ketone had reacted; the effect was most definitely observed in 51% sulfuric acid, where the reaction came to an almost complete stop after 35% of the ketone had reacted, and the iodine concentration was brought back almost to its initial value by the addition of about twenty times the usual concentration of sodium nitrite. Since the nitrite reaction causing reversal appears to increase with increasing acidity, the experiment in 66% sulfuric acid solution may be considerably in error on this account.

Because of the speed of the reaction in the stronger acid solutions, rather low initial ketone concentrations were necessary, with a large fraction of the ketone reacting. One experiment in 19% sulfuric acid showed that the introduction of a second iodine into the molecule does not become apparent until 55% of the acetophenone has reacted. (The ratio of the rate of introduction of the second iodine to that of the first is 0.033 in 19% sulfuric acid.) It was assumed that the ratio of the rates of introduction of the first and second iodines does not decrease with increasing acidity, and that it was perfectly safe to allow up to 40% of the acetophenone to react.

The procedure described previously⁵ was used for all runs except those in 30% and more concentrated sulfuric acid. In these solvents oxidation of iodide to iodine by dissolved oxygen or by sulfuric acid itself,⁸ is so fast that appreciable oxidation may take place in the fifteen minutes allowed for the solution to come to thermostat temperature, causing the iodination reaction to start prematurely. For these more concentrated solutions, the following procedure was used. A known solution of iodine in sulfuric acid was prepared in a tube of about 35-cc. capacity, with a well-fitting ground-glass stopper, by adding 25 cc. of sulfuric acid solvent from a pipet (recalibrated for each solvent) to a weighed out quantity of a known aqueous potassium iodide solution. Solid sodium nitrite (amounting to from 0.5 to 5 mg. weighed out on an analytical balance) was added, the solution stirred thoroughly, but smoothly without bubble formation, and the tube

stoppered with the stirring rod inside. The ground-glass joint was kept dry. About 9 cc. of a known solution of acetophenone in the same sulfuric acid solvent was weighed in a small weighing bottle. The two solutions were brought to temperature in the large thermostat. The reaction was started by rapidly pouring the contents of the small weighing bottle into the tube, shaking thoroughly, and pouring about 9 cc. of the resulting solution into the dry reaction cell, which previously had been mounted on the colorimeter with water at $25.00 \pm 0.01^\circ$ circulating through the water jacket. The small weighing bottle wet with the acetophenone solution was put in a large stoppered weighing bottle and weighed at leisure. The addition of the ketone solution to the iodine solution took not more than one-tenth minute. The solutions were out of a thermostat for a total of about one minute. The first reading could be taken about two minutes after mixing.

The solubility of the reaction product, phenacyl iodide, is fortunately greater (up to 3 times) under the experimental conditions in the highly acid solutions than it is in more dilute solutions.

Although iodide ion is unstable in 95% sulfuric acid, and the equilibrium concentration of iodide which can exist in such a solution is certainly very small, the iodination reaction is highly reversible in 95% sulfuric acid. In a solution saturated with iodine (*ca.* 0.0001 molar)^{6d} and 0.01 molar in acetophenone, iodination did not proceed noticeably, as measured by diminution of color perceptible to the eye, over a period of a month at room temperature. That no other reaction had intervened to prevent the iodination was shown from the following: iodine could be extracted from the solution with petroleum ether and tested for by contact with an aqueous starch-iodide solution. The acetophenone was liberated from its salt by dilution with water; the resulting solution was colorless, smelled of acetophenone, and took up freshly added iodine at approximately the correct rate (within 20%) for the acidity of the solution. A partly reacted system reverts to acetophenone in 95% sulfuric acid; phenacyl iodide, prepared in 40% sulfuric acid, was transferred first to petroleum ether solution, together with all the unreacted acetophenone but without the hydrogen iodide, and then from the petroleum ether to 95% sulfuric acid; after thirty-six hours the 95% sulfuric acid solution had approximately the full color of the iodine originally added to the 40% solution. The petroleum ether had been purified by repeated washing with 95% sulfuric acid over a period of a month, until no further color formation took place overnight with a fresh portion of sulfuric acid, followed by several distillations alternately from 95% sulfuric acid and solid sodium hydroxide. The stabilizing effect of 95% sulfuric acid on iodine at the oxidative level of I^{+6d} must mean that there is an I^+ acceptor in this solvent, which may also be able to accept I^+ from phenacyl iodide, or its conjugate acid, causing reversal of the iodination reaction.

The iodination is not catalyzed by the light source of the colorimeter in 40% sulfuric acid, since good agreement was found for duplicate runs, one with the light on throughout the run, the other with the light off except for one minute at the end of the run (after thirty minutes) when five readings were made.

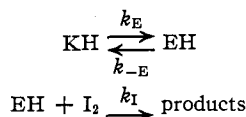
(7) Gmelins "Handbuch der anorganischen Chemie," 1933, Vol. VIII, p. 336.

(8) Smith and Mayer. THIS JOURNAL, 46, 75 (1924).

Materials.—The purification and physical constants of the materials used were described in a previous paper.⁶

Results

Kinetic Formulation.—In dilute aqueous solutions the rate of halogenation of ketones has with one exception been found independent of the concentration of the halogen and first order in ketone, which is interpreted to mean that the rate is determined by a relatively slow enolization, the enol reacting with halogen as fast as it is formed. The exception⁹ is chlorination in highly alkaline solution, in which the rate is first order in chlorinating agent (hypochlorite ion) as well as in ketone. The usual state of affairs is just reversed, and there is a rapid formation of enol or enolate ion, followed by a slow rate-determining reaction between enol or enolate ion and hypochlorite ion. A simple first order formulation fits our results in perchloric acid solutions up to and including 20%, and in sulfuric acid solutions up to and including 15%. In 51% sulfuric acid the reaction is second order. There are two possible explanations for the change in order. One is that the rate of enolization increases so rapidly that it first becomes comparable with, and finally very much greater than, the rate of iodination of the enol, so that the second step becomes rate determining. This is like the situation found by Bartlett, except that the same halogenating agent is involved in the second order as in the first order reaction. Or, perhaps the rose colored modification of iodine which begins to appear in the more concentrated acid solutions can directly iodinate the ketone without the necessity of a preliminary enolization. If this is the explanation, the order of the reaction in 51% sulfuric acid means that the direct iodination has completely supplanted iodination through the enol. For the mechanism



making no assumptions as to the relative rates of the two steps, we have the following three equations connecting the unknowns c_{KH} , c_{EH} and $c_{\text{prod.}}$, where c is concentration

$$\begin{aligned} c_{\text{KH}}^0 &= c_{\text{KH}} + c_{\text{EH}} + c_{\text{prod.}} \\ 2\Delta c_{\text{I}_2} &= c_{\text{prod.}} \\ k_E c_{\text{KH}} &= k_{-E} c_{\text{EH}} + k_I c_{\text{I}_2} c_{\text{EH}} \end{aligned}$$

c_{KH}^0 is the initial concentration of ketone. The factor 2 enters the second equation because of the presence of the sodium nitrite. The last equation represents the assumption that EH is a kinetically "unstable" intermediate.¹⁰ Substitution in the rate equation

$$-2\frac{dc_{\text{I}_2}}{dt} = k_I c_{\text{EH}} c_{\text{I}_2}$$

leads to

$$-2\frac{dc_{\text{I}_2}}{dt} = \frac{k_E(c_{\text{KH}}^0 - 2\Delta c_{\text{I}_2})c_{\text{I}_2}}{k_{-E}/k_I + c_{\text{I}_2}} \quad (1)$$

Integrating, and substituting the equation

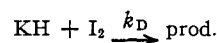
$$2m\Delta h \equiv 2\Delta c_{\text{I}_2} = \Delta c_{\text{KH}}$$

where h is the colorimeter setting, we get

$$(1 - B/A) \log \frac{c_{\text{KH}}^0/2m}{c_{\text{KH}}^0/2m - \Delta h} + B/A \log \frac{h^0}{h} = k_E t / 2.303 \quad (2)$$

$$B = k_{-E}/mk_I \quad A = c_{\text{KH}}^0/2m - h^0$$

For the second possibility, which includes the additional reaction



and the additional assumption that $k_I c_{\text{I}_2} \gg k_{-E}$ (*i. e.*, the rate of enolization is rate determining for that part of the iodination which still goes through the enol), the differential equation is

$$-2\frac{dc_{\text{I}_2}}{dt} = k_D(c_{\text{KH}}^0 - 2\Delta c_{\text{I}_2})(k_E/k_D + c_{\text{I}_2}) \quad (3)$$

The important difference between the two differential equations lies in this, that according to equation (1) the apparent order of the reaction with respect to iodine increases during the reaction, while according to equation (3) the apparent order decreases during the reaction; any reaction involving a sufficiently large change in iodine concentration cannot possibly be fitted by both these equations. The integrated form of equation (3) is very unsuccessful when applied to experiments in 39.5% sulfuric acid, in which the iodine concentration was varied more than 100-fold during the reaction; a value of k_D/k_E suitable for the high initial iodine concentrations is much too large for the low iodine concentrations near the end of the reaction.

The lowest curve in Fig. 1 is a plot of the left side of equation (2) against time, for six experiments in 39.5% sulfuric acid. The value of B used to calculate the ordinate is 11; this was selected by trial and error, using the two criteria of freedom from curvature of the plot for a single experiment, and quality of agreement of the slopes

(9) Bartlett, *This Journal*, **56**, 967 (1934); Bartlett and Vincent, *ibid.*, **57**, 1596 (1935).

(10) Skrabal, *Monatsh.*, **64**, 289 (1934).

of the plots of different experiments. Initial acetophenone concentration in these six runs ranged from 814 to 50.6×10^{-5} molar, initial iodine concentration from 49.4 to 7.24×10^{-5} molar, and the total range of iodine concentration covered was from 49.4 to 0.07×10^{-5} molar. The agreement of the data with equation (2) shows that the first explanation for the dependence of the rate on iodine concentration is the correct one.

Rate Calculations.—All the results in 30 to 51% sulfuric acid were fitted to equation (2), one

than equation (2). The two equations corresponding to equations (2) and (4) for runs showing no dependence of rate on iodine concentration already have been derived,⁵ or can be derived from equations (2) and (4), for $k_1 \gg k_{-E}$. They are listed below for purposes of reference.

$$\log [c_{KH}^0/mf - \Delta h] = -\frac{k_E}{2.303} t + \log c_{KH}^0/mf \quad (5)$$

$$h = -\frac{c_{KH}^0}{mf} k_E t + h^0 \quad (6)$$

where

$$c_{KH}^0/mf \gg \Delta h$$

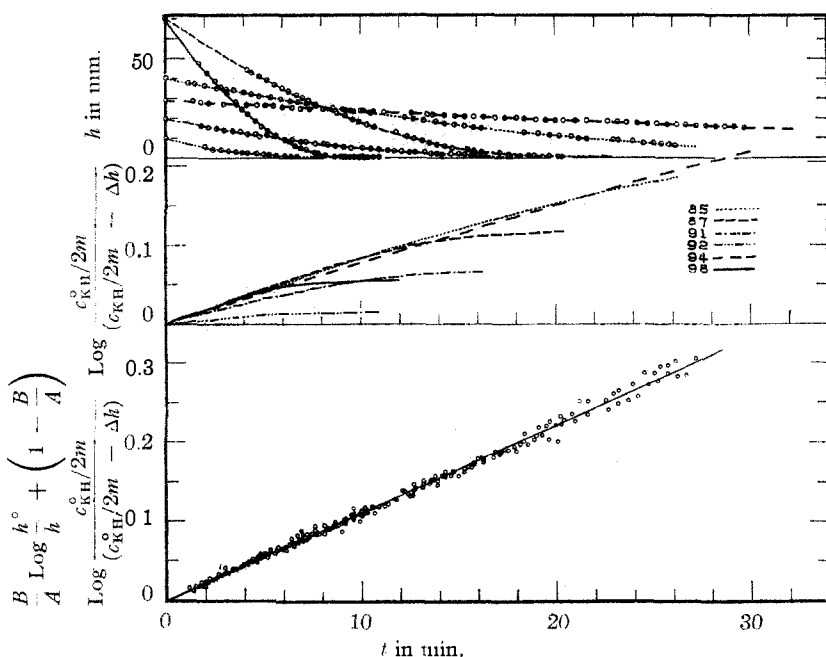


Fig. 1.

of the two unknowns in the equation being determined by trial and error in the manner described, the other calculated from the slope of the resulting plot. For each experiment the two quantities k_E and $K_E k_1$ were calculated, making use of the equation

$$K_E k_1 = \frac{k_E k_{-E}}{k_{-E} mB} = \frac{k_E}{mB}$$

In the more dilute acid solutions in which the rate is dependent on iodine concentration, it was possible to work with such high initial ketone concentrations that $c_{KH}^0/mf \gg \Delta h$ (f has the value 2 for nitrite oxidation, 2.5 for iodate oxidation) and equation (2) could be simplified to

$$h = \frac{B c_{KH}^0/2m}{A - B} \ln \frac{h^0}{h} = \frac{A c_{KH}^0/2m}{A - B} k_E t + h^0 \quad (4)$$

This equation requires much less computation

The average specific rates k_E and $K_E k_1$ for the various acid concentrations are presented in Table I. Acid concentrations of multiplicates were usually not quite identical; for averaging, the rates were all calculated to the same acid concentration, assuming the rate linear in the acid concentration. The number of experiments run with sodium nitrite is tabulated under the heading *N* and the number with potassium or sodium iodate under *I*. The precision of rates calculated by equations (5) and (6) already has been discussed⁵; where there are several multiplicates, the average deviation from the mean

is well within the assigned precision measure in all cases. The tabulated *P. M.* in per cent. was calculated by dividing the estimated average deviation from the mean by the square root of the number of experiments. Where k_E has little influence in determining the rate of the over-all reaction (46, 51% sulfuric acid), a considerable range of values of k_E will allow linear plots with very little variation in the value of $K_E k_1$, and the reverse is true when the reaction is nearly zero order in iodine. This range has been indicated in Table I. The difference between the best value and one end of this range is a maximum deviation rather than an average deviation, and is not strictly comparable with the precision measures tabulated for other runs. The experimental error certainly increases with increasing acidity. The increasing speed of the reaction reduces the number of readings which

TABLE I

RATES IN PERCHLORIC ACID SOLUTIONS AT 25.00°

% HClO ₄	No. of expts.		<i>k_E</i> (min. ⁻¹)	P. M. for <i>k_E</i> %	<i>K_Ek₁</i> (min. mol./liter) ⁻¹
	<i>I</i>	<i>N</i>			
2.091	5		0.0001565 ^a	0.5	
3.523	1		.000270	1.0	
7.16	2		.000571	0.7	
10.50	1	3	.000874	.5	
13.00	4		.001104 ^a	.5	
20.40	1	1	.001983	.7	>1350
24.90	1	2	.00276	1.0	<5000
30.20	1	3	.00394	2.0	<3000

^a Taken from ref. 5.

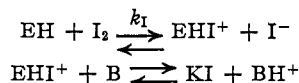
RATES IN SULFURIC ACID SOLUTIONS AT 25.00°

% H ₂ SO ₄	No. of expts.		<i>k_E</i> (min. ⁻¹)	P. M. for <i>k_E</i> %	<i>K_Ek₁</i> (min. mol./liter) ⁻¹
	<i>I</i>	<i>N</i>			
0.520	1		0.0000650	1.0	
1.069	1		.0001344	1.0	
1.586	1		.0001870	1.0	
2.100	1		.000278	1.0	
4.122	1		.000539	1.0	
5.185	1		.000755	1.0	
7.49	1		.001132	1.0	
9.90	7		.001750	0.5	>1220
13.71	1		.00280	1.0	
15.22	2		.00331	2.0	
19.00	5	3	.00521	0.4	<5000
24.40	2	1	.00856	1.0	<1950
30.78	2		.01438	2.5	570 ± 130
35.40	3		.0213 ± 0.001		420 ± 100
39.50	10		.0258 ± .004		325 ± 60
45.9	2		.051 ± .015		120 ± 10
51.0	4		>.05		62 ± 2
66	1			(4)	

can be made, and increases the importance of the error in measuring time. The method of mixing which must be used for the reactions in 30 to 51% sulfuric acid introduces further error because the time of mixing is of appreciable duration compared to the total reaction time (one- to two-tenths minute compared with six minutes or more), and during this time ketone concentration is higher than the calculated initial ketone concentration. Since equations (2) and (4) contain the absolute value of *h*, rather than only terms in Δh , the ever-present possibility of spoiling the optical balance of the colorimeter in mounting the cell at the beginning of the reaction supplies another source of error. Large errors caused by this trouble were avoided by rejecting all runs in which the calculated *h*⁰ did not lie on a smooth extrapolation of the observed *h*'s. It is necessary to include very low colorimeter settings to get sufficiently large changes in iodine concentration. The absolute error for settings below 5 mm. increases steadily above the 0.17 mm. found for settings from 45–5

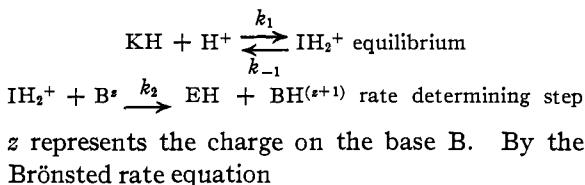
mm., and of course the percentage error in *h* becomes very large.

Effect of Increasing Acidity on *K_Ek₁*.—Values of *K_Ek₁* in sulfuric and perchloric acid solutions of the same concentration are equal, within the rather large error of measurement, and decrease steadily with increasing acidity. The mechanism of enol iodination is probably¹¹



Our experimental conditions were such that the reversal of the first step was suppressed, and *k₁* is simply the forward rate of the reaction between enol and iodine. The decrease in this rate can only be attributed to a medium effect of whose nature we are ignorant. The change in the color of the iodine-solvent complex with increasing acid concentration may be connected with a decrease in efficiency as a donor of I⁺.

Effect of Increasing Acidity on *k_E*.—The probable mechanism of the enolization is¹²



$$\frac{dc_{\text{EH}}}{dt} = \sum_{\text{B}^z} k_{2\text{B}^z} c_{\text{IH}_2^+} c_{\text{B}^z} \frac{f_{\text{IH}_2^+} f_{\text{B}^z}}{f_{[\text{X}^+]^*}}$$

where *f* is activity coefficient, [X⁺]^{*} is the activated complex [IH₂⁺·B^z]^{*}, and summation is to be taken over all bases in the solution. Then

$$k_E = \frac{1}{c_{\text{KH}}} \frac{dc_{\text{EH}}}{dt} = \sum_{\text{B}^z} k_{2\text{B}^z} \frac{c_{\text{IH}_2^+}}{c_{\text{KH}}} c_{\text{B}^z} \frac{f_{\text{IH}_2^+} f_{\text{B}^z}}{f_{[\text{X}^+]^*}} \quad (7)$$

c_{IH₂⁺}/*c_{KH}* increases with increasing acidity according to the equations

$$\frac{c_{\text{IH}_2^+}}{c_{\text{KH}}} = \frac{a_{\text{H}^+} f_{\text{KH}}}{K_{\text{KH}} f_{\text{IH}_2^+}} = \frac{K_{\text{BH}}^{(z+1)} a_{\text{BH}}^{(z+1)} f_{\text{KH}}}{K_{\text{KB}} a_{\text{B}}^z f_{\text{IH}_2^+}} = \frac{h_0}{K_{\text{KH}}}$$

where *h*₀ is the negative antilogarithm of the acidity function *H*₀². Substituting the last pair of equalities in equation (7), we arrive at the following pair of equations

$$k_E = \frac{1}{K_{\text{KH}}} \left[k_{2\text{H}_2\text{O}} c_{\text{OH}_3^+} \frac{f_{\text{KH}} f_{\text{OH}_3^+}}{f_{[\text{X}^+]^*}} + \frac{K_{\text{H}_2\text{SO}_4}}{k_{2\text{H}_2\text{O}} c_{\text{H}_2\text{SO}_4}} \frac{f_{\text{KH}} f_{\text{H}_2\text{SO}_4}}{f_{[\text{X}^+]^*}} + \dots \right] \quad (8)$$

$$k_E = \frac{1}{K_{\text{KH}}} \left[k_{2\text{H}_2\text{O}} h_0 a_{\text{H}_2\text{O}} \frac{f_{\text{IH}_2^+}}{f_{[\text{X}^+]^*}} + k_{2\text{H}_2\text{SO}_4} h_0 a_{\text{H}_2\text{SO}_4} \frac{f_{\text{IH}_2^+}}{f_{[\text{X}^+]^*}} + \dots \right] \quad (9)$$

(11) Bartlett and Tarbell, THIS JOURNAL, 58, 466 (1936).

(12) Zucker and Hammett, *ibid.*, 61, 2785 (1939); Cohn and Urey, *ibid.*, 60, 679 (1938).

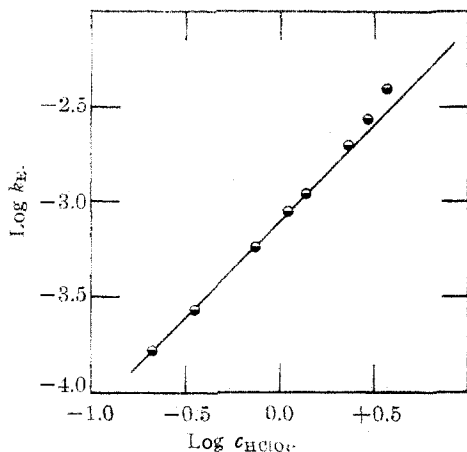


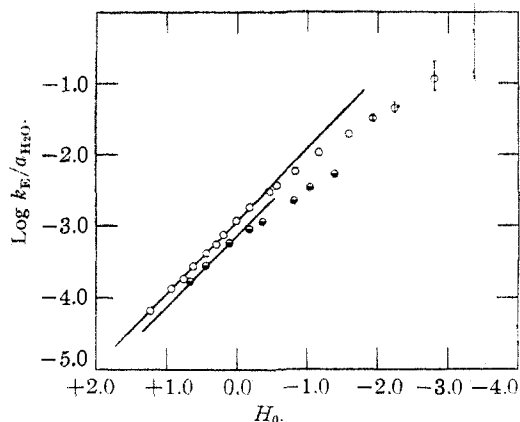
Fig. 2.

The first term in each equation represents acid catalysis by oxonium ion; the second term represents acid catalysis by bisulfate ion, and vanishes in the case of perchloric acid solutions; other terms which may enter the summation for both acids are those corresponding to catalysis by molecular acid, or by the acid conjugate to molecular acid. Bisulfate ion catalysis is very important in the sulfuric acid solutions, which therefore offer a more complicated case; this is shown by the fact that the specific rate in any sulfuric acid solution is always considerably larger than that in the perchloric acid solution of the same weight per cent., even though the two solutions are nearly identical in H_0 as well as in molarity, molality or mole fraction of any other catalyst present.

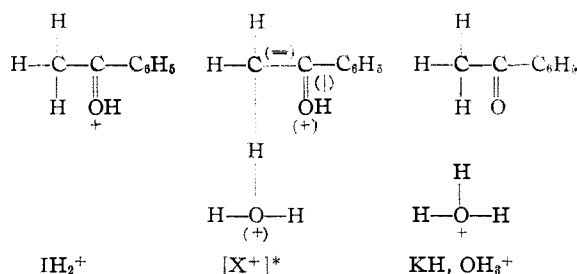
In dilute aqueous solutions the concentration of each catalyst can be determined independently; consequently the quantities of the form

$$k_{2B} z^2 \frac{f_{KH} f_{BH}^{(z+1)}}{f_{[X^{(z+1)}]^*}}$$

in equation (8) can be determined, and have been found to show a very small dependence upon the ionic strength of the medium. This is because the long range or coulombic forces which determine the activity coefficients under these conditions depend almost entirely upon the ionic charge; $f_{BH}^{(z+1)}$ therefore cancels $f_{[X^{(z+1)}]^*}$ since their charges are identical, and f_{KH} is nearly independent of medium. A similar argument would lead one to expect a cancellation of the $f_{IH_2^+}/f_{[X^+]^*}$ factor in the first term of equation (9). In more concentrated solutions in which the highly specific short range forces are important, one cannot predict any cancellation with certainty. Yet the data for the enolization in perchloric acid show a

Fig. 3.—●, Expts. in HClO₄; ○, expts. in H₂SO₄.

satisfactory proportionality to $c_{OH_3^+}$, and none to $h_0 a_{H_2O}$. This is shown in Figs. 2 and 3 in which $\log k_E$ is plotted against $\log c_{OH_3^+}$ and $\log k_E/a_{H_2O}^{13}$ is plotted against $\log h_0$, respectively. Proportionality requires a linear plot of unit slope. In terms of equations (8) and (9) this means that $f_{KH} f_{OH_3^+}/f_{[X^+]^*}$ is constant in this range of media while $f_{IH_2^+}/f_{[X^+]^*}$ is not. There must therefore be a fairly exact and complete cancellation of this type of medium effect in the one ratio which cannot take place in the other. If actual structures are compared, it is obvious that any

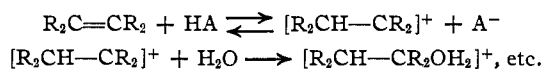


effect of the medium change specifically on the H—O—H part of $[\text{X}^+]^*$ which causes a change in the activity coefficient of $[\text{X}^+]^*$, cannot possibly be counterbalanced by any corresponding change in the activity coefficient of IH_2^+ , whereas there might be a similar change in the activity coefficient of the oxonium ion. If one can generalize from this case, it must be possible to factor the activity coefficient, at least roughly, into one factor due to charge and another for each of the several parts of the molecule.

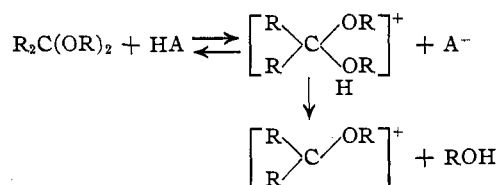
The relative degree of dependence on changing acid concentration of the two types of activity coefficient ratio involved in the comparison of

(13) Values of a_{H_2O} obtained from Pearce and Nelson, THIS JOURNAL, 55, 3075 (1933).

rates with the two acidity measures may throw some light on the detailed nature of the rate-determining step of any acid-catalyzed reaction. There are three possibilities: (a) the rate determining step is a proton transfer as it is in the enolization; (b) it involves a water molecule in some other way than as a base, as in the following possible mechanism for the acid catalyzed hydration of an olefin



(c) it involves a spontaneous cleavage or other change of the conjugate acid of the substrate, as is possible in the acetal hydrolysis



In case (a) equations similar in form to (8) and (9) can always be derived; if the first rather than the second proton transfer is rate determining, k_1 is substituted for k_2/K_S , and $[X^+]*$ is $[S \cdot OH_3^+]*$ instead of $[SH^+ \cdot OH_2]*$, where S is substrate. All such reactions are subject to general acid catalysis. In case (b) the proper equations are the first terms only of the series in (8) and (9). The only possible catalyst is oxonium ion, no matter what the solvent. In case (c) we have the following pair of equations

$$\begin{aligned} -\frac{1}{c_s} \frac{dc_s}{dt} &= k_a = \frac{k}{K_S} \frac{c_{OH_3^+}}{a_{H_2O}} \frac{f_S f_{OH_3^+}}{f_{[SH^+]*}} \\ &= \frac{k}{K_S} h_0 \frac{f_{SH^+}}{f_{[SH^+]*}} \end{aligned}$$

This type can show catalysis by the solvated proton only; in water the catalyst is oxonium ion, in 100% sulfuric acid it is $H_3SO_4^+$, etc. The last two types are usually not differentiated and are called together specific hydrogen ion catalysis; however, only the last is a true specific hydrogen ion catalysis in all solvents and the other might be called specific oxonium ion catalysis.

If general acid catalysis can be demonstrated for a reaction, it must have a mechanism of the first type. A reaction for which only oxonium ion catalysis can be demonstrated in aqueous solutions may belong in any one of the three classes. But if the reaction is in either of the first two classes, the activated complex contains a molecule of water, $f_S f_{OH_3^+} / f_{[SHOH_2^+]*}$ should be

more independent of changing acidity than $f_{SH^+} / f_{[SHOH_2^+]*}$, and $c_{OH_3^+}$ should be a better measure of acidity than h_0 . And if the reaction is in the third class, $f_{SH^+} / f_{[SH^+]*}$ should be more independent of changing medium than $f_S f_{OH_3^+} / f_{[SH^+]*}$, and h_0 should be a better measure of acidity than $c_{OH_3^+}$. In order to apply this criterion it is necessary to know the rates in solutions in which h_0 can be measured,² and in which $c_{OH_3^+}$ is known—*i. e.*, aqueous perchloric, hydrochloric or nitric acids. It is also necessary to carry the rate measurements into a region where h_0 and $c_{OH_3^+}$ are different. h_0 equals $c_{OH_3^+}$ for all these acids within the error of measurement of h_0 up to about 1 molar acid; it is only in more concentrated acid that h_0 becomes greater than $c_{OH_3^+}$, and not before about 1.5 molar acid that a very marked and rapidly increasing divergence sets in. By this criterion the hydrolyses of sucrose and of cyanamide belong to the third class, while that of ethyl acetate has not been studied in sufficiently acid solutions to make an unambiguous determination possible.³

Nachod¹⁴ observed a decrease in the apparent equilibrium constant for the enolization of acetyl acetone with increasing concentration of hydrochloric acid in methanol solution. He suggested by way of explanation the formation of a coordination compound between ketone and acid, $R_2C=O \cdot H \cdot A$. If such a reaction took place with acetophenone in the solutions in which the iodination was studied, both k_E and $K_E k_1$ as defined could be expected to have a different dependence on the acidity of the solution than that previously derived, assuming no coordination. However, there are several reasons why this is unlikely. Hydrogen bonding of the sort suggested should cause any equilibrium constant involving the ketone, calculated for the total apparent ketone concentration, to vary with changing acidity; the effect should appear in the basic ionization constant as well as in the enolization constant, yet the ionization constant of acetophenone is independent of acidity over the entire region of ionization (55–86% sulfuric acid).¹⁵ Coordination should cause the solubility of a ketone to increase with increasing acidity; actually the solubility of acetophenone decreases with increasing concentration of sulfuric acid and of perchloric acid, at least up to 1 molar solutions. And, finally, the phenomenon observed by Nachod cannot be of

(14) Nachod, *Z. physik. Chem.*, **A182**, 193 (1938).

(15) Flexser, Hammett and Dingwall, *ibid.*, **57**, 2103 (1935).

very widespread occurrence among ketones, because the enolization constant of acetoacetic ester (which is much more closely related structurally to the ketones studied by Nachod than is acetophenone), has been calculated from kinetic data for hydrochloric acid solutions from 0 to 0.370 molar,¹⁶ and the values show no trend with increasing acidity.

Summary

The iodination of acetophenone has been studied in 2 to 30% aqueous perchloric acid solutions, and in 0.5 to 66% aqueous sulfuric acid

(16) Pedersen, *J. Phys. Chem.*, **57**, 751 (1934).

solutions. The rate is determined by the rate of enolization of acetophenone in the more dilute acid solutions, and by the rate of reaction of the enol with iodine in 51% and more concentrated sulfuric acid solutions; at intermediate acidities these two rates are of comparable magnitudes.

Even in the simplest case, in aqueous perchloric acid solutions, the enolization rate is not proportional to h_0 , but is proportional over a considerable range to c_{OH^+} . Reactions whose rates are directly proportional to h_0 , when this is varied widely, are probably examples of specific hydrogen ion catalysis, and not of general acid catalysis.

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Molecular Rotation and Polymorphism in the *t*-Butyl Halides

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A variety of roughly spherical molecules from methane to camphor is found to possess rotational freedom in the solid state, as well as polymorphic transitions at temperatures below which such freedom is generally lost.^{1,2} The lower isomeric alkyl halides provide opportunity for studying the effect of structure on crystal form and molecular freedom in simple polar lattices by dielectric and optical measurements.^{3,4} The tertiary butyl halides are the most symmetrical members of this series, and, despite their considerable dipole moments resulting from the dissimilar groups, they behave as spherical molecules in such a kinetic process as viscous flow.³ Also, electron diffraction results on *t*-butyl chloride⁵ indicate no appreciable distortion of the usual tetrahedral arrangement. The data of the present report on these compounds also may be compared with similar studies on the hydrogen halides.⁶⁻⁹

Preparation and Purification of Materials.—The final purification of the chloride and bromide was fractionation in an 80 × 2 cm. Pyrex glass column, packed with beads, wrapped, and jacketed. It had a still head equipped for reflux ratio control. Temperatures were measured by

short-range Anschütz type thermometers previously calibrated by the Bureau of Standards. The *t*-butyl iodide sample finally was distilled through a shorter Vigreux-type column under reduced pressure. Refractive indices were obtained from a Pulfrich refractometer. Immediately upon distillation the samples were frozen and kept in the dark until the dielectric measurements were begun.

***t*-Butyl Chloride.**—The compound was prepared by the method of "Organic Syntheses,"¹⁰ from *t*-butyl alcohol and hydrochloric acid. The usual precautions of neutralization and washing were followed by prolonged drying over calcium chloride. The product was twice fractionally distilled; b. p. 50.60°; f. p. -24.6°; $n_{\text{D}}^{20.0}$ 1.38470. Material recrystallized from its own melt gave the same constants. Recent literature values give b. p. 51.0°,¹¹ and the refractive index noted above lies between the reported values 1.38528¹² and 1.3839.¹³

***t*-Butyl Bromide.**—As with the chloride, this compound was distilled from a mixture having the proportions of one mole of *t*-butyl alcohol and two moles of constant-boiling hydrobromic acid. After washing, it was dried for several days over anhydrous calcium bromide, and was thrice fractionated. Successive middle fractions had the same refractive index: b. p. 73.2°, f. p. -17.7°, $n_{\text{D}}^{20.0}$ 1.42757. A separately prepared lot gave the same refractive index, and boiled at 73.3°. The best literature values include: b. p. 73.25°,¹¹ n_{D}^{20} 1.4275-1.4277.¹⁴

***t*-Butyl Iodide.**—The Eastman Kodak Co. product was distilled repeatedly under reduced pressure after thorough drying. Even though the best fractions came over colorless and were at once frozen, a light straw color always

- (1) Smyth, *Chem. Rev.*, **19**, 329 (1936).
- (2) Eucken, *Z. Elektrochem.*, **45**, 126 (1939).
- (3) Baker and Smyth, *THIS JOURNAL*, **61**, 1695 (1939).
- (4) Baker and Smyth, *ibid.*, **61**, 2063 (1939).
- (5) Beach and Stevenson, *ibid.*, **60**, 475 (1938).
- (6) Smyth and Hitchcock, *ibid.*, **55**, 1830 (1933).
- (7) Hettner and Pohlman, *Z. Physik*, **108**, 45 (1937).
- (8) Damkohler, *Ann. Physik*, **81**, 76 (1938).
- (9) Kruis and Kaischew, *Z. physik. Chem.*, **B41**, 427 (1939).

(10) Gilman, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1928, Vol. VI11, p. 50.

(11) Timmermans and Delcourt, *J. chim. phys.*, **31**, 85 (1934).

(12) Smyth and Dornte, *THIS JOURNAL*, **53**, 545 (1931).

(13) Kistiakowsky and Stauffer, *ibid.*, **59**, 165 (1937).

(14) Kharasch and Potts, *ibid.*, **58**, 57 (1936).