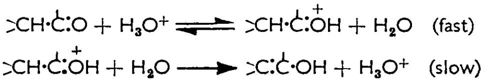
654. *Kinetics of the Bromination of Acetone in Concentrated Aqueous Hydrochloric Acid.*

By G. Archer and R. P. Bell.

The rate of bromination (and hence of enolization) of acetone has been measured in 1—8M-aqueous hydrochloric acid. After correction for the proportion of acetone present in the protonated form the reaction velocity is found to depend much more closely on the acidity function than on the acid concentration, in contrast to expectations for this type of reaction. This result casts some doubt on the use of acidity-dependence as a criterion of mechanism.

The rate of bromination or iodination of ketones in dilute solutions of strong acids is independent of the concentration of halogen and directly proportional to that of hydrogen ions. The usually accepted mechanism is



$$\mathrm{>CH\cdot C\!:\!O + H_3O^+ \rightleftharpoons >CH\cdot C\!:\!\overset{+}{O}H + H_2O} \quad \text{(fast)}$$

$$\mathrm{>CH\cdot C\!:\!\overset{+}{O}H + H_2O \longrightarrow >C\!:\!C\cdot OH + H_3O^+} \quad \text{(slow)}$$

followed by rapid halogenation of the enol. This mechanism is highly probable, since proton transfers to and from oxygen atoms are known to take place rapidly, and it is supported by the fact that the substitution of deuterium oxide for water increases the reaction velocity,[1] an effect which would be difficult to explain in any other way. Attempts have also been made to obtain evidence as to mechanism from measurements of reaction velocity at high concentrations of acid. According to a hypothesis first put forward by Zucker and Hammett,[2] if the transition state is formed simply by the addition of a proton to the substrate, then the reaction velocity will be closely proportional to the acidity function h_0, but if (as in the above mechanism) the transition state also contains a water molecule, then the reaction velocity will increase less rapidly than h_0 and may be approximately proportional to the hydrogen-ion concentration. The experimental evidence for the general validity of this distinction has been recently reviewed by Long and Paul.[3] The evidence relating to the enolization of ketones is rather meagre. Zucker and Hammett [4] studied the iodination of acetophenone in aqueous perchloric acid up to 3·6M, but found that at higher acidities the rate was no longer independent of iodine concentration. More recently, Satchell [5] has measured the rate of iodination of acetone in aqueous hydrochloric acid up to 2·7M. Both papers report that the reaction velocity is more closely proportional to $[H_3O^+]$ than to h_0, but the measurements do not extend to very high concentrations, and, as will be seen later, there are some problems about their interpretation. The present paper describes measurements of the rate of bromination of acetone in 1—8M-aqueous hydrochloric acid.

Experimental

All materials were of " AnalaR " grade, and hydrochloric acid solutions were standardized against borax. The course of the reaction was followed by observing the temperature change in the apparatus previously described for the thermal maximum method.[6,7] The reaction was started by breaking a small bulb of bromine solution in 50 c.c. of acetone solution, the concentration of hydrochloric acid being the same in both solutions. The concentration of acetone

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[1] Reitz, *Z. Elektrochem.*, 1937, **43**, 659; *Z. phys. Chem.*, 1937, **179**, A, 119.

[2] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2785.

[3] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.

[4] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.

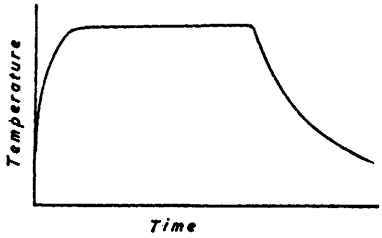
[5] Satchell, *J.*, 1957, 2878.

[6] Bell and Clunie, *Proc. Roy. Soc.*, 1952, *A*, **212**, 16.

[7] Bell, Gold, Hilton, and Rand, *Discuss. Faraday Soc.*, 1954, **17**, 151.

was at least 50 times that of bromine, so that the reaction followed a zero-order course. The plots of galvanometer reading against time resembled the Figure, where the almost horizontal portion represents a steady state in which the rate of heat production by the reaction is equal to the rate of heat loss to the thermostat. The break in the curve corresponds to the point at which all the bromine is used up and the temperature begins to fall: in our experiments the first-order cooling constant was about 0·08 sec.$^{-1}$. Galvanometer readings were taken every 2 sec. and recorded by means of a dictaphone. The velocity constants were calculated from the time at which the break in the curve occurs: this varied between 30 and 100 sec., and could be located with an accuracy of 1—2 sec. Variations in bromine concentration by a factor of two produced no significant change in the velocity constants, thus confirming the zero-order character of the reaction.

Some of the earlier experiments showed poor reproducibility and gave curves differing in form from the Figure. This was traced to the formation in acid solutions of acetone of appreciable amounts of mesityl oxide, which reacts with bromine much more rapidly than does acetone. Mesityl oxide absorbs strongly at 243 mμ in aqueous solution ($\varepsilon = 8600$; in approximate agreement with earlier workers [8]), and this could be used to determine its concentration. Its formation could be minimized by keeping the acetone concentration fairly low, and by adding the acetone to the acid solution only just before the addition of bromine. An interval of about 2 min. was necessary to attain thermal equilibrium, and tests showed that after this time the amount of mesityl oxide formed never exceeded 5% of the amount of bromine used in the reaction.



The experimental results are given in the first three columns of the Table. Each velocity constant is the mean of three separate determinations, which had an average deviation of ±1%. The first-order constant for enolization is calculated on the assumption (justifiable under our conditions) that each molecule of acetone reacts with one molecule of bromine.

Rate of enolization (bromination) of acetone in aqueous hydrochloric acid at 25°.
k = first-order velocity constant in sec.$^{-1}$. c = concentration in moles/l.

c (acetone)	c (HCl)	10^5k	c (HCl) (corr.)	$-H_0$	$-\log\{k(K_{SH^+} + h_0)/h_0K_{SH^+}\}$
0·430	1·00	3·68	0·98	0·19	4·90
0·430	2·00	8·38	1·95	0·67	5·00
0·218	3·00	15·2	2·95	1·03	5·04
0·218	4·00	23·8	3·92	1·37	5·08
0·218	5·00	34·0	4·87	1·71	5·11
0·218	6·00	53·2	5·84	2·06	5·03
0·132	7·00	72·6	6·88	2·51	4·97
0·132	8·00	112	7·87	2·96	4·82

DISCUSSION

The velocity constants in the Table are about 10% greater than those obtained by Dawson and Powis [9] in 1M-hydrochloric acid and by Satchell [5] in the range 1—3M. This discrepancy is somewhat greater than the estimated experimental uncertainties, and is probably due to formation of mesityl oxide. However, the uncertainty is not great enough to affect the general nature of the relation between rate and acid concentration.

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[8] Nagakura, Minegishi, and Stanfield, *J. Amer. Chem. Soc.*, 1957, **79**, 1033.
[9] Dawson and Powis, *J.*, 1913, 2135.

If log k is plotted against H_0 or $-\log c$ neither plot is a straight line of unit slope, but the discrepancy is smaller for $-\log c$ than for H_0, in agreement with the findings of Zucker and Hammett[4] and of Satchell[5] at lower concentrations. However, this type of plot is appropriate only when the extent of protonation of the substrate is small, and this is certainly not the case at the acidities used in our experiments. Recent spectrophotometric measurements[8] give $\mathrm{p}K_{\mathrm{SH^+}} = -1{\cdot}58$ for the ion $\mathrm{Me_2C{:}OH^+}$, and this value corresponds to a 5—95% protonation of acetone in 1—8M-hydrochloric acid. Under these conditions the observed velocity constants must be multiplied by $([\mathrm{S}] + [\mathrm{SH^+}])/[\mathrm{S}]$ before comparison with the acidity function or the acid concentration, and if we make the assumptions about activity coefficients which are implicit in the acidity function concept this correction factor becomes $(K_{\mathrm{SH^+}} + h_0)/K_{\mathrm{SH^+}}$. A further small correction is necessary because the acid concentration is decreased by the formation of $\mathrm{SH^+}$: the corrected acid concentrations are given in the fourth column of the Table, and the values of H_0 in the fifth column correspond to these corrected concentrations, the data collected by Paul and Long[11] being used.

If the corrected velocity constant is proportional to the acidity function h_0, then the quantity in the last column should be independent of concentration. It does in fact vary slightly, but shows no consistent trend with concentration. On the other hand, proportionality between the corrected velocity and the acid concentration should give a constant value to $-\log \{k(K_{\mathrm{SH^+}} + h_0)/cK_{\mathrm{SH^+}}\}$, and this quantity increases steadily by two logarithmic units as the concentration increases. Our results thus indicate that the reaction rate is related to the acidity function rather than to the acid concentration, in contrast to the accepted view for this type of reaction. If Satchell's results[5] are corrected in the same way for the protonation of the acetone they fall just half way between linear dependence on h_0 and on c, but the acid concentrations are not high enough for the deviations to be great.

Since the mechanism of acid-catalyzed enolization is well established[12] the above results throw considerable doubt upon the validity of Zucker and Hammett's hypothesis for reactions in which the transition state contains a water molecule. Similar conclusions have been reached on the basis of the effect of pressure on some acid-catalyzed reactions,[13] where the observed volume of activation suggests the mechanism A-2, while the parallelism with h_0 indicates A-1. This hypothesis admittedly has little theoretical basis, and has been put forward on the basis of experimental evidence. Our own results show that when there is a considerable degree of protonation the observed velocity constant may be approximately proportional to the acid concentration although the corrected velocity follows the acidity function closely, and it would be desirable to obtain direct evidence of the degree of protonation in other reactions which appear to follow the acid concentration. However, as pointed out by Long and Paul,[3] the effect of acid concentration on the reaction velocity may depend upon the part played by the water molecule in the transition state. In acid-catalyzed enolization it is acting as a base in removing a proton from the $\equiv$CH group, while in other reactions (*e.g.*, the acid hydrolysis of esters) it becomes attached to carbon by a nucleophilic displacement. It may well be that these different modes of attack correspond to different behaviour in the activity coefficients of the transition state, but further experimental evidence is needed.

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[10] Long and Paul, reference 3; Schubert and Latourette, *J. Amer. Chem. Soc.*, 1952, **74**, 1829.

[11] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

[12] For recent confirmation by a study of deuterated ketones, see Swain, Di Milo, and Cordner, *J. Amer. Chem. Soc.*, 1958, **80**, 5983.

[13] Koskikallio and Whalley, *Trans. Faraday Soc.*, 1959, **55**, 815.