**133.** *Kinetics of the Halogenation of Acetone in Alkaline Solutions.*

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Measurements have been made of the rate of reaction of acetone with alkaline hypobromite and hypoiodite solutions at $0°$, $10°$, $18°$, and $25°$. The reaction is of zero order with respect to halogenating agent, and of first order with respect to both acetone and hydroxyl ions : hence it is concluded that the rate-determining step is the transfer of a proton from the acetone molecule to the hydroxyl ion. Comparison with other data indicates that in this type of reaction a change of substrate or catalyst is reflected primarily in a change in activation energy, though this behaviour is not common to all protolytic reactions.

ACETONE reacts with alkaline solutions of halogens according to the equation

$$CH_3 \cdot CO \cdot CH_3 + 3OX^- \longrightarrow CH_3 \cdot CO \cdot O^- + CHX_3 + 2OH^-.$$
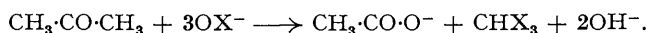
It was shown by Bartlett (*J. Amer. Chem. Soc.*, 1934, **56**, 967) that with hypobromite and hypoiodite solutions containing excess of hydroxyl ions the reaction velocity is independent of the concentration of halogenating agent, and has the same value for iodine and bromine. The same behaviour is found in the base-catalysed halogenation of acetone in less alkaline solutions, where the product is tribromo- or tri-iodo-acetone. These products may well be intermediates in the haloform reaction, and in any case the rate-determining step is probably the same in the two cases, *i.e.*, the transfer of a proton from the acetone molecule to the basic catalysts present (cf., *e.g.*, Bell, " Acid-Base Catalysis," Oxford, 1941, p. 135). Bartlett records only three not very concordant experiments at $0°$, and the present paper describes more extended measurements over a range of temperatures.

EXPERIMENTAL.

Most of the reactions were carried out with hypobromite solutions, which were made by adding to a solution of sodium hydroxide of known concentration an amount of bromine sufficient to convert part of it into hypobromite. (The initial concentration of hypohalite was about $0·005M$ in all experiments; this proved sufficient to maintain the reaction order at unity₁) 2 C.c. of this solution were pipetted into each of ten tubes in the thermostat. To the first tube was added 1 c.c. of a solution of potassium iodide in N-hydrochloric acid, and the liberated iodine titrated with N/200-thiosulphate (micro-burette) : this served to determine the concentration of hypobromite, and hence also that of free hydroxyl ions remaining. To each of the remaining tubes was added 1 c.c. of approximately $0·002M$-acetone solution, using an automatic pipette (Bell, Lidwell, and Vaughan-Jackson, *J.*, 1936, 1794). At one-minute intervals $0·5$ c.c. of potassium iodide in N-hydrochloric acid was added to successive tubes to stop the reaction and to convert the remaining hypobromite into iodine, which was titrated with N/200-thiosulphate. One tube was left for about 40 minutes and used to determine the final hypobromite concentration.

It is reasonable to suppose that the hydroxyl ion is the only effective basic catalyst present, and the results obtained confirm this. Hydroxyl ions are produced during the reaction, but in most experiments this can be allowed for with sufficient accuracy by taking the mean of the initial and final values of [OH]. In these cases the plot of $\log_{10}(x - x_\infty)$ against t (minutes) gave a straight line, where x is the thiosulphate titre at time t, and x_∞ the final titre. The catalytic constant of the hydroxyl ion, k_{OH^-}, has been previously defined (Bell and Lidwell, *Proc. Roy. Soc.*, 1940, **176**, *A*, 87)

as the rate of disappearance of halogen in moles per litre per minute in a solution which is molar with respect to both acetone and hydroxyl ions. Since three moles of halogen react with one of acetone, we have

$$k_{OH^-}[OH] = 3 \times 2 \cdot 303 \ d \log_{10} (x - x_\infty)/dt,$$

which equation was used to obtain most of the constants in Table I. In a few cases the observed value of x_∞ was checked by calculation from the known weight of acetone used in making up the solutions : there was agreement within experimental error.

The above method of calculation is applicable only when the acetone concentration is a small fraction of the hydroxyl-ion concentration. When this is not the case the correct kinetic equation is $dy/dt = k_{OH^-}(a - y)(b + 2y)$, where a and b are the initial concentrations of acetone and hydroxyl ions respectively, and $a - y$ is the acetone concentration after time t. The integrated equation is

$$(b - 2a)k_{OH^-} \cdot t = 3 \times 2 \cdot 303 \log_{10} \{a(b + 2y)/b(a - y)\}$$

and this was used to obtain the values marked with an asterisk in Table I, a, b, and y being all directly calculable from the observed titres.

The experiment marked † in the table was carried out with hypoiodite solution instead of hypobromite. In this case the plot of $\log_{10} (x - x_\infty)$ against t was a straight line for approximately the first two-thirds of the reaction, and then fell off rapidly. This is probably due to the conversion of hypoiodite into iodate (known to be rapid in alkaline solution), resulting in a hypoiodite concentration so low that it is unable to react with the acetone anions as fast as they are formed. However, this change to iodate does not render invalid the use of the thiosulphate titre as a measure of the extent of the reaction, since the conversion of hypoiodite to iodate does not affect the amount of iodine liberated in acid solution.

Table I.

Acetone concentration approx. 0·00077M throughout; [OH$^-$] = initial concentration of hydroxyl ions.

Temp.						
25°	$\{$ [OH$^-$]	0·0068	0·0147	0·0153	0·0353	
	$\{$ k_{OH^-}	29·0 *	31·2 †	31·8	32·6	Mean 31·2 (Calc. : 31·6)
18°	$\{$ [OH$^-$]	0·0119	0·0165	0·0274	0·0469	
	$\{$ k_{OH^-}	18·3 *	19·1	18·7	18·7	Mean 18·7 (Calc. : 18·5)
10°	$\{$ [OH$^-$]	0·0122	0·0209	0·0307	0·0410	
	$\{$ k_{OH^-}	8·8 *	10·8	9·7	9·3	Mean 9·6 (Calc. : 9·6)
0·07°	$\{$ [OH$^-$]	0·0419	0·0789	0·0819		
	$\{$ k_{OH^-}	3·96	4·07	4·12		Mean 4·07 (Calc. : 4·07)

Discussion.

The above results confirm Bartlett's findings (*loc. cit.*) that the reaction velocity is independent of the halogen concentration, and the same for bromine and iodine. Our value of k_{OH^-} at 0·07° (4·07) agrees well with the mean of the three values given by Bartlett for 0° (4·38, 3·93, 3·72). It should be possible to compare our value of k_{OH^-} at 25° (31·2) with values derived from measurements in buffer solutions. However, the latter values are unreliable, since in buffer solutions only a small fraction of the observed velocity is due to hydroxyl-ion catalysis, and the calculation of the hydroxyl-ion concentration is subject to uncertainties in the values to be assigned to dissociation constants and activity coefficients. The only data at all suitable are those of Dawson and Key (*J.*, 1928, 543) on phosphate buffers, and of Bell and Lidwell (*loc. cit.*, p. 88) on trichlorophenoxide buffers. Dawson and Key give k_{OH^-} = 26, but a recalculation of their results using more recent data on phosphate buffers gives k_{OH^-} = 17. Bell and Lidwell derived k_{OH^-} = 15, using the pH values of the trichlorophenoxide buffers observed with a glass electrode. However, measurements with a hydrogen electrode (Ogston, *J.*, 1936, 1713) give $3 \cdot 2 \times 10^{-6}$ as the dissociation constant of trichlorophenol, and using this value the same data give k_{OH^-} = 34. Moreover, the measurements with trichlorophenol are subject to some uncertainty because trichlorophenol itself reacts slowly with iodine, and a correction has to be applied to allow for this reaction. Our measurements in alkaline solutions thus give a value of k_{OH^-} which is of the same order of magnitude as values derived from buffer solutions, but is much more reliable.

The calculated values of k_{OH^-} in Table I are derived from the equation

$$k_{OH^-} = 2 \cdot 09 \times 10^{11} \ \exp. \ (- 13,400/RT),$$

and it is seen that the Arrhenius equation $k = A e^{-E/RT}$ is closely obeyed. It is of interest to compare the values of A and E with those found for the halogenation of acetone and of ethyl acetoacetate, catalysed by acetate ions (data from Smith, *J.*, 1934, 1744; Pedersen, *J. Physical Chem.*, 1934, 38, 501). The best comparison is in terms of the ionisation velocity k', and in deriving k' from the halogenation velocities it must be remembered that the initial ionisation is followed by the rapid introduction of three and two halogen atoms for acetone and ethyl acetoacetate respectively. The comparable ionisation velocities are therefore obtained by dividing the halogenation velocities by 3 and by 2 respectively. The results are given in Table II.

Table II.

Constants of the Arrhenius equation.

Catalyst.	Substrate.	k' (25°).	E.	$A \times 10^{-11}$.
OH$^-$	Acetone	10·4	13,400	0·7
CH$_3$·CO·O$^-$	Acetone	$2 \cdot 4 \times 10^{-6}$	22,800	1·3
CH$_3$·CO·O$^-$	Ethyl acetoacetate	29	13,400	1·7

The variations in A are probably within experimental error, and certainly the major part of the effect of changing the catalyst or the substrate appears in the activation energy rather than in the factor A.

The same kind of behaviour had been previously found for changes of catalyst in the anion-catalysed decomposition of nitramide (Baughan and Bell, *Proc. Roy. Soc.*, 1937, **158**, *A*, 464) : on the other hand, Smith found in the acid-catalysed iodination of acetone (*loc. cit.*) and the base-catalysed mutarotation of glucose (Smith and Smith, *J.*, 1937, 1413) that changes of catalyst were reflected in the factor A rather than in the activation energy. It is difficult to estimate the accuracy of Smith's conclusions, since most of his temperature coefficients were derived indirectly from composite velocity constants at two temperatures only. However, it is unlikely that either type of simple behaviour will apply to protolytic reactions in general, since it is well known that in a series of acid–base equilibria, changes in equilibrium constant cannot be correlated with either energy changes or entropy changes taken separately (cf. Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380). These equilibria involve two opposed protolytic reactions, and any simple correlation between the reaction velocity and either A or E must fail for at least one of these reactions.