175. *Kinetics of the Bromination of Acetone in Aqueous Solution.*

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The kinetics of the bromination of acetone in aqueous solution have been studied at very low bromine concentrations. Velocity constants are derived for the reaction of molecular bromine and tribromide ion with the enol of acetone, and these are compared with constants for related reactions.

The halogenation of acetone in aqueous solution is normally of zero order with respect to halogen, being determined by the rate of ionization or enolization of the acetone, but by working with very low concentrations of chlorine, Bell and Yates [1] were able to measure the rate of reaction of the enol with chlorine. A few experiments on bromination gave an approximate rate for the corresponding reaction with bromine, which was found to be considerably faster than the reaction with chlorine, but the effect of bromide-ion concentration was not studied, and it was not established that the bromine concentrations used were low enough to make the halogenation reaction completely rate-determining. The present Paper describes a more thorough investigation.

Experimental

Water was redistilled from alkaline potassium permanganate in an all-glass still, to remove reducing impurities. Sodium bromide was recrystallized from water. Other materials were of AnalaR grade. AnalaR hydrobromic acid was diluted to *ca.* 0·1M, and free bromine then removed by bubbling oxygen-free nitrogen through the boiling solution for 30—40 min. It was cooled to room temperature, with continued passage of nitrogen, and stored in a dark glass bottle; after four days, measurements of the redox potential did not show the presence of any free bromine.

The rates of bromination were measured at 25° by following the change in redox potential at a platinum-gauze electrode relative to a standard glass electrode, as previously described.[2] The acetone concentration was throughout *ca.* 0·003M, and the initial bromine concentration was 10^{-6}M or lower; thus the acetone concentration remained effectively constant during an

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[1] Bell and Yates, *J.*, 1962, 1927.

[2] Bell and Atkinson, *J.*, 1963, 3260.

experiment. All measurements were made in acid solution, and under these conditions any further bromination of monobromoacetone can be neglected.[3] The bromine concentration was followed down to 10^{-8}M—10^{-9}M. The absolute bromine concentrations were derived from the observed e.m.f. by standardizing with a known amount of bromine at the end of each experiment, as previously described.[2]

With a fresh acetone solution, the plot of e.m.f. (E) against time (t) showed a small initial rapid fall, as previously observed for chlorination.[1] This is attributable to a very small amount of impurity, since, when several experiments were made with one acetone solution by successive additions of bromine, only the first experiment showed the initial drop. The subsequent E–t plots were initially concave to the time axis, but tended to a constant slope after a fall of about 30 mv. This suggests a reaction order between zero and unity with respect to bromine. With the assumption (justified subsequently) that the enolate ion is not involved as an intermediate, the reaction scheme is:

$$\mathrm{HS} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{SH};\ \mathrm{SH} + \mathrm{Br_2}^* \xrightarrow{k} \text{Products}$$

where HS and SH represent the keto and enol forms of acetone, and Br_2* represents any brominating species, in this instance Br_2 and Br_3^-. k_1 and k_{-1} depend upon the catalysts present in the solution, and, under conditions of acid catalysis, $k_1 = k_{\mathrm{H}}[\mathrm{H}^+]$. As previously shown,[4] if [HS] is constant this reaction scheme leads to the integrated equation:

$$t + ([\mathrm{Br_2}^*]/k_{\mathrm{H}}[\mathrm{H}^+][\mathrm{HS}]) = -2FE/k\boldsymbol{R}TK_{\mathrm{E}}[\mathrm{HS}] + \text{const.},$$

where $K_{\mathrm{E}} = k_1/k_{-1}$ is the equilibrium proportion of enol in aqueous acetone. A plot of E against the left-hand side of this equation should therefore give a straight line of slope $-k\boldsymbol{R}TK_{\mathrm{E}}[\mathrm{HS}]/2F$, whence k can be determined. k_{H} is known to be $2{\cdot}84 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ from several concordant investigations at higher concentrations of chlorine, bromine or, iodine,[1,5–10] and when this value was used excellent straight lines were obtained over a range of at least 60 mv. In calculating k from the slopes we have taken $K_{\mathrm{E}} = 2{\cdot}0 \times 10^{-6}$, as observed by Schwarzenbach and Wittwer[11] for aqueous solutions of acetone which had stood for several hours.* The values of k thus obtained are collected in the Table.

Bromination of aqueous acetone solutions at 25°.

k = second-order velocity constant, in l. mole^{-1} sec.$^{-1}$.

			$10^{-5}k$	
10^3[HClO$_4$] (M)	10^3[HBr] (M)	10^3[NaBr] (M)	obs.	calc.
0	100	0	59, 58, 57	57
0	50	50	57, 61, 61	57
0	20	80	57, 57, 56	57
0	10	90	57, 57, 58	57
100	0	100	56, 56, 56	57
50	0	150	51, 49, 51	50
150	0	50	69, 69, 68	69

DISCUSSION

The observed second-order constant at $[\mathrm{Br}^-] = 0{\cdot}1$M is somewhat greater than that given by Bell and Yates[1] ($5{\cdot}0 \times 10^6$ l. mole^{-1} sec.$^{-1}$, recalculated with $K_{\mathrm{E}} = 2{\cdot}0 \times 10^6$). This is because the earlier work assumed the bromination step to be wholly rate-determining, which is not actually the case until the bromine concentration has fallen to about 10^{-7}M. The first five rows of the Table refer to a constant bromide concentration, and show

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* In the previous paper[1] we took $K_{\mathrm{E}} = 2{\cdot}5 \times 10^{-6}$; this was determined in freshly prepared aqueous solutions of acetone, and will be less close to the equilibrium value.

[3] Bell and Lidwell, *Proc. Roy. Soc.*, 1940, *A*, **176**, 88.

[4] Bell and Rawlinson, *J.*, 1961, 726.

[5] Rice and Fryling, *J. Amer. Chem. Soc.*, 1925, **47**, 382.

[6] Dawson and Key, *J.*, 1928, 2154.

[7] Smith, *J.*, 1934, 744.

[8] Reitz, *Z. phys. Chem.*, 1937, **179**, 119.

[9] Rice and Kilpatrick, *J. Amer. Chem. Soc.*, 1923, **45**, 1401.

[10] Dawson, *Trans. Faraday Soc.*, 1928, **24**, 640.

[11] Schwarzenbach and Wittwer, *Helv. Chim. Acta*, 1947, **30**, 569.

that the rate is independent of acidity over the range $[H^+] = 0{\cdot}01$—$0{\cdot}1$M, thus confirming the assumption that bromination involves only the enol and not the enolate ion. The dependence of rate on bromide ion (at a constant ionic strength $I = 0{\cdot}2$), shown in the last three rows of the Table, enables separate rate constants k_2 and k_2' to be assigned to the species Br_2 and Br_3^-. It is easily shown that

$$k(1 + K[\mathrm{Br}^-]) = k_2 + k_2'K[\mathrm{Br}^-],$$

where $K = [\mathrm{Br}_3^-]/[\mathrm{Br}_2][\mathrm{Br}^-] = 16$.[12] The last column of the Table gives the values of k calculated from this equation with $k_2 = 1{\cdot}03 \times 10^7$ l. mole^{-1} sec.$^{-1}$, $k_2' = 2{\cdot}8 \times 10^6$ l. mole^{-1} sec.$^{-1}$.

The constant for Br_2 is about ten times as great as that found previously[1] for Cl_2, though the comparison is not a strict one since the chlorination experiments were carried out at an ionic strength $I = 1{\cdot}5$ compared with $I = 0{\cdot}2$ in the present work. Similar relative reactivities were found in the halogenation of diethyl malonate,[1,4] where bromine was 30 and 4 times as reactive as chlorine towards the enol and enolate ion, respectively. Our present results show bromine to be about four times as reactive as the tribromide ion towards the enol of acetone; the corresponding factor is 6 for the less reactive enols of diethyl malonate and methyl methanetricarboxylate,[4] and 1·6 for their more reactive enolate ions. All these comparisons illustrate the general principle that the selectivity between different reagents becomes less as the reactivity of the organic species increases.

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[12] Jones and Baeckstrom, *J. Amer. Chem. Soc.*, 1934, **56**, 1517.