205. *Bromination of Acetone in Alkaline Solution at Low Temperatures.*

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The bromination of acetone catalysed by hydroxide ion has been investigated in 6·7M-sodium perchlorate solution between −25 and +20°. A curved Arrhenius plot is obtained. This curvature is probably not due to proton tunnelling, as the hydrogen-isotope effect on the Arrhenius parameters is small, and the Arrhenius plot for hexadeutero-acetone is curved, but may be ascribed to a specific medium effect.

A CURVED Arrhenius plot obtained in the bromination of di-isopropyl ketone in alkaline solution has been cited as evidence for proton tunnelling.[1] The bromination of acetone in alkaline solution is a similar type of reaction whose kinetics have already been investigated at 25°.[2] Acetone, unlike di-isopropyl ketone, is readily soluble in water, and so it is possible to use concentrated salt solutions as the solvent to reach temperatures considerably below 0° without fear of salting out the substrate. The medium chosen is 6·7M-sodium perchlorate. This is the eutectic composition and freezes at —32°.[3]

The bromination of acetone in alkaline conditions obeys the integrated rate equation

$$kt = \frac{3}{b + 2a} \log_e \frac{a(b + 2x)}{b(a - x)}$$

for the disappearance of hypobromite ion; a is the initial concentration of acetone, b that of the hydroxide ion, and x is the quantity of acetone used after time t. (The original Paper by Bell and Longuet-Higgins [2] reads $b - 2a$ instead of $b + 2a$.)

The hydrogen isotope effect in this reaction will not be simple. Both primary and secondary isotope effects should arise when hexadeuteroacetone is used as the substrate. The ratio k_H/k_D should therefore be large. The secondary isotope effects should also influence the Arrhenius parameters, so that precise predictions of the limits for classical behaviour cannot be made. However, a large difference between the activation energies for deuteron and proton transfer and a large ratio of the pre-exponential factors of the Arrhenius equation would indicate tunnelling.[4]

EXPERIMENTAL

Materials.—Acetone (B.D.H.) was dried (K_2CO_3) and distilled. Hexadeuteroacetone (Merk Fine Chemical Co., Canada) was stated to contain 98·2% [$^2H_6$]acetone and 1·8% [$^2H_5$]acetone. Sodium perchlorate (B.D.H.) was recrystallized from water above 80°, to deposit the anhydrous salt,[5] dried at 120°, and stored over phosphoric oxide. All other reagents were AnalaR.

Method.—The reaction was followed by titration,[2] hypobromite ion remaining after various times being estimated by addition of potassium iodide after acidification, and titration of the iodine liberated against standard thiosulphate. Infinity values were obtained similarly from a sample left to react at room temperature for at least nine half-lives.

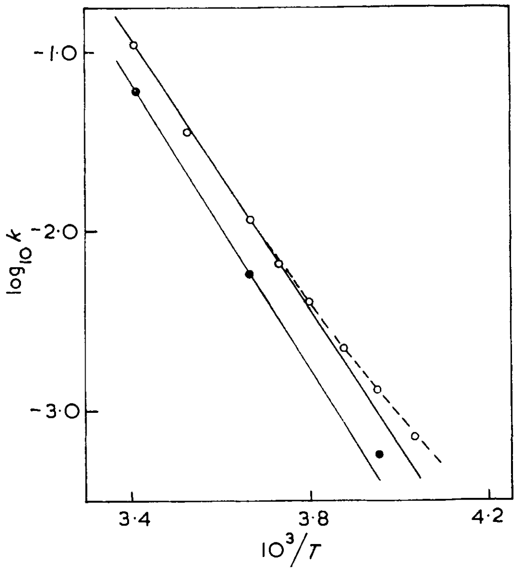
The low-temperature thermostat was described by Hulett.[6]

RESULTS

Each rate constant (Table 1), derived from runs providing eight points with conversions up to 75%, is the mean of 4—6 determinations, with a maximum standard deviation of less than 3%. The first Arrhenius equation at the head of Table 1 represents the best fit to the four points at the highest temperature. The curvature of the plot (Figure) can be estimated from the

[1] Hulett, *J.*, 1965, 430.
[2] Bell and Longuet-Higgins, *J.*, 1946, 636.
[3] Freeth, *Rec. Trav. chim.*, 1924, **43**, 475.
[4] Bell, *Proc. Roy. Soc.*, 1933, *A*, **139**, 466; 1935, *A*, **148**, 241.
[5] Scaife and Tyrrell, *J.*, 1958, 386.
[6] Hulett, *Proc. Roy. Soc.*, 1959, *A*, **251**, 274.

difference between the observed rate constant and that calculated from this equation. This is shown in the column $k_{\text{obs}}/k_{\text{calc}}$, where the ratio at the lowest temperature is 1·55. The second Arrhenius equation in k' is a forced fit to all the points in the plot; the column headed $k_{\text{obs}}/k'_{\text{calc}}$ indicates that it fits the results badly, with divergencies up to four times the maximum experimental error. These discrepancies are systematic, corresponding to the curvature of the plot, so it is not possible to fit the results to an Arrhenius equation.



Arrhenius plot. Open circles are experimental points for acetone. Full circles are experimental points for [$^2H_6$]acetone, displaced upwards by 0·8 unit. Full line is $\log_{10} k_{\text{calc}}$. Broken line is $\log_{10} k_q$.

TABLE 1.

Bromination of acetone in 6·7M-NaClO$_4$.

$k = 1{\cdot}18 \times 10^{12} \exp(-17480/\boldsymbol{R}T)$ l.mole^{-1} sec.$^{-1}$.

$k' = 8{\cdot}69 \times 10^{10} \exp(-16020/\boldsymbol{R}T)$ l.mole^{-1} sec.$^{-1}$.

Temp.	10^3k (obs.)	10^3k (calc.)	$10^3k'$ (calc.)	10^3k_q	$\frac{k_{\text{obs}}}{k_{\text{calc}}}$	$\frac{k_{\text{obs}}}{k'_{\text{calc}}}$	$\frac{k_{\text{obs}}}{k_q}$
20·0°	108·6	107·4	96·7	107·4	1·011	1·123	1·011
10·0	36·5	37·2	36·6	37·0	0·981	0·997	0·986
−0·3	11·5	11·5	12·5	11·8	1·000	0·920	0·975
−5·0	6·57	6·52	7·42	6·95	1·008	0·885	0·946
−10·0	4·11	3·50	4·19	3·94	1·174	0·981	1·043
−15·0	2·23	1·83	2·31	2·24	1·219	0·965	0·995
−20·0	1·31	0·932	1·25	1·28	1·406	1·048	1·023
−25·0	0·716	0·462	0·655	0·760	1·550	1·093	0·942

Three experiments were performed with hexadeuteroacetone; as this was scarce, only one run could be done at each temperature (Table 2).

TABLE 2.

Bromination of hexadeuteroacetone in 6·7M-NaClO$_4$.

$k = 6{\cdot}10 \times 10^{11} \exp(-18500/\boldsymbol{R}T)$ l.mole^{-1} sec.$^{-1}$.

Temp.	−20·0°	−0·3°	20·0°
10^4k_{obs}	0·898	8·95	95·4
10^4k_{calc}	0·626	8·95	95·4

The deviation of the point at −20° from the Arrhenius line through the two other points is about 43%, compared with 41% for the point at the same temperature for acetone.

DISCUSSION

Extrapolation of the results for the acetone to 25° gives the second-order rate constant $k = 0{\cdot}178$ l. mole^{-1} sec.$^{-1}$ (Bell and Longuet-Higgins[2] give $k = 0{\cdot}53$). The smallness of this value is probably due to the effect of the very high salt concentration on the transition state. This salt effect is only about one third of that observed in the solvent-catalysed bromination of 2-ethoxycarbonylcyclopentanone[7] in 5·2M-NaBr. The effect in the latter case was probably much more marked because the solvent itself was one of the reactants.

Curved Arrhenius plots in the direction observed may be ascribed to a number of causes.[8] Thermodynamic effects, in which the change in specific heat on activation is not zero, are usually too small to detect on a conventional Arrhenius plot. Large curvatures may be found where the reaction is complex, but this reaction is controlled by a simple proton transfer.[2] Two major reasons remain: proton tunnelling or a specific medium effect.

Proton tunnelling has been invoked to explain this curvature for other simple proton transfer reactions.[1,6,9,10] If it applies here, the barrier dimensions derived from Bell's equations for a parabolic energy barrier[11] should have feasible values. The quantum correction Q in the form

$$Q = \frac{\pi\alpha/\beta}{\sin \pi\alpha/\beta} - \frac{\alpha \exp{(\alpha - \beta)}}{\beta - \alpha}$$

has been used, where $\alpha = E^*/\boldsymbol{k}T$ and $\beta = 2\pi^2 a\,(2mE^*)^{\frac{1}{2}}/\boldsymbol{h}$. E^* is the height of the energy barrier whose base is $2a$, and m is the mass of the proton.

E^* and a were calculated by a method of trial and error to give rate constants in agreement with the experimental values over the whole temperature range. The values of k_q so calculated, using $E^* = 20{\cdot}5$ kcal. mole^{-1} and $a = 0{\cdot}671$ Å are shown in Table 1 and as the broken line in the Figure. The discrepancies can be judged from k_{obs}/k_q, which lies within 0·942—1·043, indicating a divergence of less than twice the experimental error which varies randomly with temperature. The quantum mechanical treatment therefore appears to give satisfactory agreement with the experimental results.

The ratio E/E^* so calculated is 0·85. This lies between those for the hydroxide-ion catalysed bromination of di-isopropyl ketone[1] and the fluoride-ion catalysed bromination of 2-ethoxycarbonylcyclopentanone[5,12] on the one hand, and those for the latter reaction catalysed by water and chloroacetate ion on the other.[5,12] Curvature of the Arrhenius plot was observed in the former cases[1,6] but not in the latter. The half-width of the parabola, a, is also reasonable, being somewhat larger than those found previously in dilute aqueous solutions,[1,12] but rather smaller than those in concentrated salt solutions[1,6] or in alcoholic solution.[9,10] It appears therefore that the curvature of the Arrhenius plot here is consistent with proton tunnelling.

If this conclusion is correct, the reaction should show large kinetic isotope effects. The results of the few experiments performed are shown in Table 3. The ratio of the rate constants is very large. This includes both the primary isotope effect due to the differences in rupture of either a C–H or a C–D bond, and the secondary effect of neighbouring C–H or C–D bonds on the reaction centre. In such a reaction, Swain,

TABLE 3.

Isotope effects in the bromination of acetone in 6·7M-NaClO$_4$.

k_H/k_D at 20°	$E_D - E_H$	A_D/A_H
11·4	1020 cal. mole^{-1}	0·52

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[7] Hulett, *Trans. Faraday Soc.*, 1963, **59**, 1815.
[8] Hulett, *Quart. Reviews*, 1964, **18**, 227.
[9] Caldin and Harbron, *J.*, 1962, 3454.
[10] Caldin and Kasparian, private communication.
[11] Bell, *Trans. Faraday Soc.*, 1959, **55**, 1.
[12] Bell, Fendley, and Hulett, *Proc. Roy. Soc.*, 1956, *A*, **235**, 453.

di Milo, and Cordner[13] suggested that the role of the base is to facilitate the shift of the electron pair from the incipient proton to the carbon atom. Thus a strong anionic base will render the rupture of the C–H bond in the transition state more complete, and so will bring out more fully the differences between the C–H and C–D bonds. It would therefore be expected that the isotope effect should be larger for catalysis by hydroxide ion than by acetate ion. Reitz obtained $k_H/k_D = 7$ for the acetate ion catalysed reaction,[14] so that the present result for hydroxide ion, 11·4, is not unexpected. This is in contrast to Pocker's recent figure, 7.[15] Thus, while proton tunnelling might lead to a large kinetic isotope effect, it would not be impossible to explain the observed value in classical terms.

The Arrhenius parameters for the reaction with $[^2H_6]$acetone are derived on the assumption that the curve is linear between 0 and 20°. This is reasonable as the curve for acetone is linear in this range. If the curvature of the plot for acetone were due to tunnelling alone, that for hexadeuteroacetone would be straight. The isotope effects on the Arrhenius parameters (Table 3) therefore are most probably correct, but represent minimum values in the unlikely event that curvature occurs between 0 and 20°.

The difference in the activation energies of about 1 kcal. mole^{-1} is well within the difference in zero point energies of C–D and C–H bonds, and the ratio $A_D/A_H = 0{\cdot}52$ is very small, in contrast to the value 24 observed in the bromination of 2-ethoxycarbonylcyclopentanone.[12] These results therefore, although probably subject to large uncertainties, are well within the range compatible with classical proton transfer.

The curvature of the Arrhenius plot, despite the reasonable values of the barrier dimensions derived from it, should not be ascribed to proton tunnelling. This conclusion is strengthened by the almost parallel curvature indicated in the plot for deuteron transfer. These results show the importance of confirming the interpretation of curved Arrhenius plots by a study of isotope effects.

The curvature may be ascribed to a specific medium effect which occurs in both the proton and deuteron transfer reactions, and probably only operates in water well below its normal freezing point. At these low temperatures fairly long-lived ice-like conglomerates may form in the water, possibly, but not necessarily, associated with the ions of the salt. A hydroxide ion relatively distant from a substrate molecule may fit into this water structure, and, by a type of charge transfer process through the pseudo-ice similar to that invoked to explain the high proton and hydroxide ion conductance in ice,[16] could appear close to the reaction centre, and so contribute to the overall rate. This effect would be relatively more important at low temperatures, and so the fall in rate is less rapid than is required by the Arrhenius equation. There is no evidence that such reasoning applies to hydroxide ion catalysis in dilute aqueous solution above 0°, as linear Arrhenius plots are usually obtained under such conditions—presumably the " ice-bergs " are too short lived at such temperatures—and so the curvature noted in the bromination of di-isopropyl ketone is not to be explained in this way.[1] This effect will also be specific to ions which can be formed by self-ionisation of the solvent, and so will not apply to the fluoride-ion catalysed bromination of 2-ethoxycarbonylcyclopentanone at —20°.[6]

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[13] Swain, di Milo, and Cordner, *J. Amer. Chem. Soc.*, 1958, **80**, 5983.
[14] Reitz, *Z. phys. Chem.*, 1936, *A*, **176**, 363; *A*, **177**, 834.
[15] Pocker, *Chem. and Ind.*, 1959, **87**, 1383.
[16] Conway, Bockris, and Linton, *J. Chem. Phys.*, 1956, **24**, 834.