

The Influence of the Solvent on Reaction Velocity

XI. Alkaline Hydrolysis of Ethyl Bromide in Acetone-Water Mixtures

EERO TOMMILA and P. J. ANTIKAINEN

Institute of Chemistry, University of Helsinki, Helsinki, Finland

In contrast to the uncatalysed hydrolysis of alkyl halides, the reaction between ethyl bromide and hydroxyl ion, $\text{EtBr} + \text{OH}^- \rightarrow \text{EtOH} + \text{Br}^-$, in acetone-water is little affected by changes in the proportion of water in the solvent. The specific reaction rate increases slightly with an increasing proportion of acetone up to 18-27 wt. % acetone; there is a marked decrease of the rate constant at higher acetone contents, the position of the maximum being dependent on temperature. For about 18 wt. % acetone *E* and *A* show a maximum, whereas in solvolysis they pass through a minimum. This difference in behaviour is explained by the fact that in the latter case the transition state is more polar than the initial state and that for the reaction between ethyl bromide and hydroxyl ion the transition state is less polar than the initial state of the reactants, which means that the solvation phenomena are mainly opposite in the two cases. The isodielectric activation energies and frequency factors do not differ essentially from *E* and *A* for solvents of constant composition, whereas in the case of the uncatalysed hydrolysis they are quite different in magnitude and in behaviour.

It was found in a previous investigation¹ that very interesting details are revealed in the uncatalysed hydrolysis (solvolysis) of primary and tertiary alkyl halides when water in the solvent is progressively replaced by acetone. Investigations in this field have been continued, and the present paper reports results for the alkaline hydrolysis of ethyl bromide in acetone-water mixtures. The alkaline hydrolysis of methyl and ethyl iodides has previously been studied in methanol-water and in ethanol-water mixtures by Lobry de Bruyn and Steger², but at 25° only. They found that the reaction rate increases somewhat with increasing proportion of alcohol in the solvent.

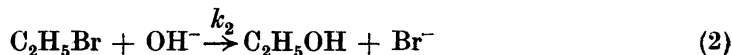
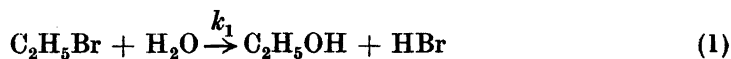
EXPERIMENTAL

Chemicals. The ethyl bromide used was a commercial specimen of the highest purity. It was carefully distilled before use. The acetone was Merck's acetone *pro analysi*. The water used as the solvent in the kinetic experiments was freshly distilled.

Method. The kinetic experiments were carried out in about 12-ml ampoules of Pyrex glass. Because of the great volatility of ethyl bromide, the same method was used as in the previous investigation. Samples of 10 ml (7–9 in each run) of a 0.05 *N* sodium hydroxide solution in the appropriate solvent were measured with a pipette into the ampoules and of ethyl bromide a quantity required to form a 0.05 *M* concentration was added into each ampoule by means of an 'Aglä' micrometer syringe equipped with a needle of fine bore. Blank experiments confirmed that ethyl bromide could be so measured into the solution with an accuracy of ± 0.1 mg. Ampoules were sealed and placed into the thermostat. At suitable intervals they were removed, quickly chilled by immersing into a mixture of ice and water, and opened, and the contents were washed into a slight excess of 0.1 *N* HCl-solution, pre-cooled in ice-water. The acid was titrated with 0.025 *N* sodium hydroxide solution, using cresol red as indicator. Because of the poor solubility of ethyl bromide in the highly aqueous solvents, a vigorous shaking of the ampoules before immersing into the thermostat was necessary. Shorter reaction times than one hour were not used. The error caused by the evaporation of ethyl bromide into the small gas volume (1–2 ml) over the solution in the ampoules was negligible.

CALCULATIONS

In alkaline solutions the following two reactions occur simultaneously



Thus, if x is the concentration of inorganic bromide after the time t , and a is the initial concentration of ethyl bromide, and b that of sodium hydroxide, the rate equation is

$$\frac{dx}{dt} = k_2(a-x)(b-x) + k_1(a-x) \quad (3)$$

For $a = b$ we have

$$\frac{dx}{dt} = k_2(a-x)^2 + k_1(a-x) \quad (4)$$

On the basis of this equation we obtain³ for evaluation of k_2 :

$$\frac{x}{a} = \frac{1 - e^{-k_1 t}}{1 - a e^{-k_1 t}} \quad (5)$$

where

$$a = \frac{a}{a + k_1/k_2} \quad (6)$$

$$\text{Equation (5) gives } a = \frac{e^{-k_1 t} + \frac{x}{a} - 1}{\frac{x}{a} \cdot e^{-k_1 t}} \quad (7)$$

If k_1 is separately determined, a can be obtained from this equation. Thus we obtain from equation (6).

$$k_2 = \frac{k_1 a}{a(1-a)} \quad (8)$$

Table 1. The applicability of equation (8). Solvent 27.2 wt. % aqueous acetone. Temperature 60.20° C.

| Time secs. | HCl 0.1012 N ml | NaOH 0.0248 N ml | $\frac{x}{a}$ | $e^{-k_1 t}$ | α | |
|---------------|-----------------------|------------------------|---------------|--------------|----------|---|
| 3 600 | 4.5 | 1.90 | 0.1834 | 0.9712 | 0.8681 | $k_1 = 8.12 \times 10^{-6} \text{ sec.}^{-1}$ $\alpha_{\text{mean}} = 0.8788$ $k_2 = 117.5 \times 10^{-5}$ (mole/l) ⁻¹ sec. ⁻¹ |
| 5 400 | 4.5 | 3.45 | 0.2602 | 0.9572 | 0.8727 | |
| 7 200 | 4.5 | 4.99 | 0.3367 | 0.9434 | 0.8819 | |
| 9 000 | 4.0 | 3.93 | 0.3852 | 0.9296 | 0.8791 | |
| 11 100 | 4.0 | 4.85 | 0.4309 | 0.9138 | 0.8753 | |
| 12 600 | 3.5 | 3.90 | 0.4840 | 0.9025 | 0.8848 | |
| 13 500 | 3.5 | 4.47 | 0.5130 | 0.8472 | 0.8912 | |
| 28 500 | 3.0 | 5.72 | 0.6860 | 0.7958 | 0.8826 | |
| 30 000 | 3.0 | 6.21 | 0.7003 | 0.7862 | 0.8836 | |

For the calculation, the values of k_1 were taken from the paper of Tommila, Tiilikainen, and Voipio¹.

As an illustration of the results the run given in Table 1 may be taken.

Side by side with the nucleophilic substitution there occurs an olefin-forming elimination. Under the conditions in the kinetic experiments performed in this investigation the proportion of the olefin-formation, however, is negligible^{4,5} (see also Ref.⁶).

The solvolysis with water is somewhat dependent on the initial concentration of ethyl bromide; in 46 wt. % acetone at 60° C, for example, the following values were found:

| | | | | |
|--|------|------|------|------|
| Initial concentration of EtBr, moles/liter | 0.2 | 0.1 | 0.05 | 0.01 |
| $10^6 k_1 \text{ sec.}^{-1}$ | 4.54 | 4.94 | 5.04 | 5.26 |

In Eq. (3) the variation of k_1 with respect to concentration is ignored. For the alkaline hydrolysis at the same temperature and in the same solvent it was found that for the initial concentration of the reactants 0.05 mole/l, $k_2 = 8.82 \cdot 10^{-4}$, and for 0.025 mole/l, $k_2 = 1.00 \cdot 10^{-4} \text{ l mole}^{-1} \text{ sec}^{-1}$. Consequently, all the experiments referred to in the discussion were conducted with equal initial concentrations, 0.05 M, for both EtBr and NaOH.

All velocity constants k_2 were corrected for a change of concentration due to thermal expansion of the solvent⁷. Activation energies, E , and frequency factors, A , were obtained from the variation of $\log k$ with $1/T$, the method of least squares being used in the calculations. The entropy of activation, ΔS^* , was calculated by means of the equation

$$A = e \frac{kT}{h} e^{\Delta S^*/R}$$

The results are summarized in Table 2.

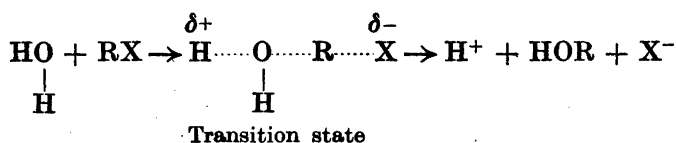
Table 2. The reaction $\text{EtBr} + \text{OH}^- \rightarrow \text{EtOH} + \text{Br}^-$ in various acetone-water mixtures.

| H_2O ml/l | Me_2CO wt. % | x_{acet} | $10^5 k$ (mole/l) $^{-1}$ sec. $^{-1}$ | | | | | E cal. | log A | $\frac{\Delta S^\ddagger}{\text{E.U.}}$ |
|------------------------------|---------------------------------|-------------------|--|--------|--------|--------|--------|-------------|---------|---|
| | | | 24.90° | 39.75° | 49.90° | 60.20° | 75.00° | | | |
| 1 000 | 0* | 0 | 1.59 | 8.00 | 22.7 | 64.4 | 222 | 20 450 | 10.19 | -13.9 |
| 900 | 8.7 | 0.029 | 2.28 | 12.7 | 32.4 | 103 | 398 | 21 200 | 10.90 | -10.6 |
| 800 | 17.8 | 0.063 | 2.63 | 13.7 | 48.6 | 138 | 529 | 22 000 | 11.50 | -7.9 |
| 700 | 27.2 | 0.104 | 2.83 | 15.6 | 43.3 | 121 | 482 | 21 100 | 10.91 | -10.6 |
| 600 | 36.5 | 0.151 | 2.79 | 14.3 | 42.8 | 104 | 444 | 20 750 | 10.65 | -11.8 |
| 500 | 46.2 | 0.210 | 2.49 | 12.8 | 35.0 | 91.5 | 347 | 20 300 | 10.30 | -13.3 |
| 400 | 56.0 | 0.283 | 2.38 | 12.2 | 32.6 | 85.0 | 314 | 20 050 | 10.08 | -14.4 |

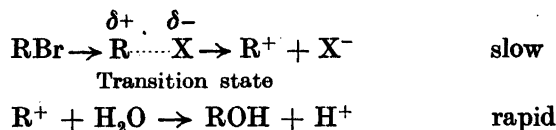
* By extrapolation.

DISCUSSION

The uncatalysed hydrolysis of n -alkyl halides is a one-stage (S_N2) reaction

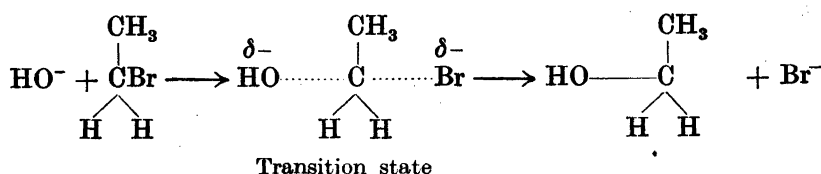


and that of tertiary alkyl halides a two-stage (S_N1) process in which the rate-determining step is the dissociation of the alkyl halide molecule:



In both reactions the transition state involves a partial separation of electric charges and is, accordingly, more polar than the initial state. Consequently, the transition state is solvated more than the inactivated alkyl halide. The charges of the transition state tend to orientate also adjacent strongly polar acetone molecules, and thus an addition of acetone to the water increases the total solvation of the transition state, which causes a decrease in E and A . For about 20 wt. % acetone E and A show a minimum¹.

In the reaction between ethyl bromide and hydroxyl ion a distribution of the charge is involved in the transition state, which is thus less polar than the initial state of the reactants:



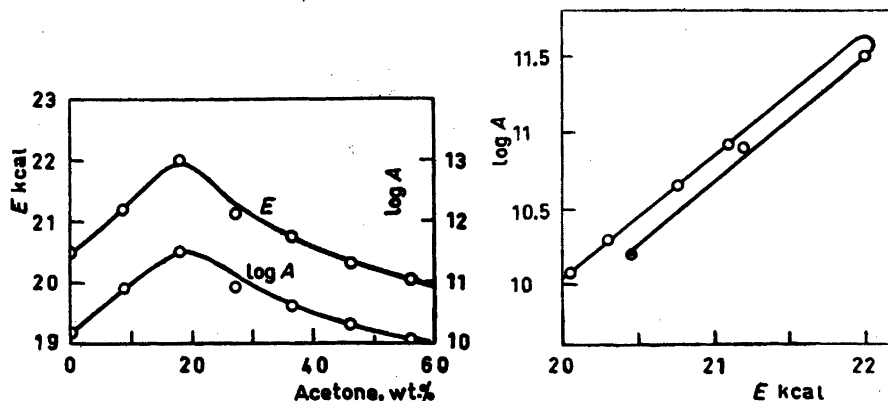


Fig. 1. Variation of E and $\log A$ with the proportion of acetone in the solvent.

Fig. 2. Plot of $\log A$ against E . \odot Water.

Owing to its lower polarity the transition state is less solvated than the initial state. With increasing proportion of acetone in the solvent the total solvation of the reactants increases more than that of the less polar transition state since the electric field of the hydroxyl ion tends to organize acetone molecules more than the weaker field of the transition state. Thus E and A should increase on adding acetone to the solvent. This is in agreement with the observed solvent effect. Table 2 and Fig. 1 show that E and A are increased on increasing the proportion of acetone until the solvent contains acetone about 18 wt.%, but that after that they have a descending slope. The alkyl group of the transition state will attach acetone molecules for which they have a specific attraction and this effect increases with the proportion of acetone in the solvent, whereas the solvation of hydroxyl ions with water becomes gradually weaker. Both of these two factors tend to decrease E and A . With increasing proportion of acetone in the solvent also the solvation of ethyl bromide increases, but it is reasonable to assume that in very dilute solutions of ethyl bromide the situation is soon reached where each alkyl halide molecule has around itself a maximum number, or nearly so, of acetone molecules and that after that their number or orientation increases only little. Changes in the internal structure of the solvent may also be of consequence. It is noteworthy that the maximum lies at about the same acetone percentage as the minimum which has been observed in the case of the uncatalysed hydrolysis. The difference in polarity between the initial state of the reactants and the transition state is smaller than in the uncatalysed hydrolysis of ethyl bromide, and correspondingly the height of the maximum, with regard to the value of E in pure water (1 500 cal) is much smaller than the depth of the minimum (5 000 cal) in the latter case.

The rate constant is little affected by changes in the composition of the solvent. On adding acetone to the water, k first increases, but then turns into decreasing. The position of the maximum velocity is dependent on temperature (Table 2). The influences of the changes in the activation energy and activation entropy on k are counteracting, and it is interesting that the entropy

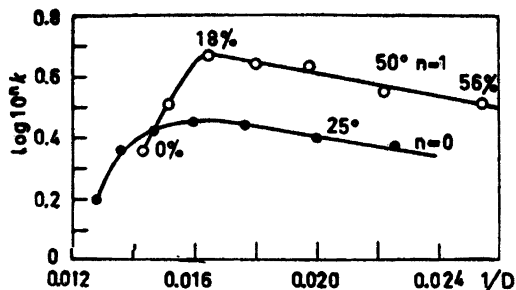


Fig. 3. Graph to show the correlation between $\log k$ and $1/D$.

changes always dominate the rate changes. The activation energy is less than that found for the solvolysis except in the region of the maximum, but since the frequency factor is much higher than that (*i. e.* $A/[H_2O]$) for the solvolysis, the rate of the reaction between hydroxyl ion and ethyl bromide is always greater than that between water and ethyl bromide. On either side of the maximum the relationship between $\log A$ and E is linear, $\Delta \log A/\Delta E$ 0.80, *i. e.* of the same order of magnitude as for the alkaline hydrolysis of carboxylic esters between pure water and the minimum (Fig. 2).

According to Laidler and Eyring⁸, for a reaction between an ion and a neutral molecule a straight line of a positive slope should be obtained for the plot of $\log k$ against $1/D$, provided the non-electrostatic effects can be neglected. The predicted change of rate with the dielectric constant⁹ in the reactions between alkyl halides and hydroxyl ion seems, according to the results of de Bruyn and Steger, to exist in alcohol-water mixtures. In acetone-water, in the region from pure water to 18–27 wt. % acetone the direction of the effect is that predicted by the theory (Fig. 3), but the plot is not linear. In mixtures containing more acetone the plot is linear, but of a negative slope, which should imply that the radius of the transition state is less than that of the OH⁻ ion. According to Amis and Jaffé¹⁰, for a reaction between a negative ion and a dipole an increase of the dielectric constant should cause an increase in reaction velocity.

Isodielectric solutions. The values of $\log k$ for isodielectric solutions at different temperatures were obtained from the k values of Table 2 by graphical interpolation, using for the dielectric constant, D , values given by Åkerlöf⁹. The linear relationship between $\log k$ and $1/T$ was found to hold also for iso-

Table 3. Isodielectric activation energies and frequency factors.

| D | 40 | 45 | 50 | 55 | 60 | 65 |
|------------|--------|--------|--------|--------|--------|--------|
| E_D cal. | 20 500 | 21 000 | 21 500 | 22 000 | 21 650 | 20 450 |
| $\log A_D$ | 10.40 | 10.78 | 11.15 | 11.53 | 11.31 | 10.44 |

dielectric solutions. In the calculation of the isodielectric activation energies, E_D , and frequency factors, A_D , only temperatures of 25°, 40°, 50°, and 60° were taken into account, since for 75° the extrapolated values of the dielectric constant are very inexact. A comparison of Tables 2 and 3 shows that the isodielectric activation energies and frequency factors do not essentially differ from those for the solvents of constant composition, and what is more, they pass through a maximum. In this respect, the reaction between ethyl bromide and hydroxyl ion differs greatly from the uncatalysed water hydrolysis of alkyl halides, in which E and E_D , and A and A_D in their magnitude and behaviour differ essentially from each other.

REFERENCES

1. Tommila, E., Tiilikainen, M., and Voipio, A. *Ann. Acad. Sci. Fennicae. A II* (1955) No. 65.
2. Lobry de Bruyn, C. A. and Steger, E. *Rec. trav. chim.* 18 (1899) 4, 311; *Chem. Zentr.* 70 II (1899) 861.
3. Moelwyn-Hughes, E. A. *Physical Chemistry*, Cambridge University Press 1940, p. 640.
4. Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, Bell and Sons Ltd. London 1953, p. 346; Chapter VIII.
5. de la Mare, P. B. D. *Annual Reports on the Progress of Chemistry* 47 (1950) 134.
6. Grant, G. H. and Hinshelwood, C. N. *J. Chem. Soc.* 1933 258.
7. Koskikallio, J. *Ann. Acad. Sci. Fennicae A II* (1954) No. 57.
8. Laidler, K. J. and Eyring, H. *Ann. N.Y. Acad. Sci.* 39 (1940) 303.
9. Åkerlöf, G. *J. Am. Chem. Soc.* 54 (1932) 4125.
10. Amis, E. S. *Kinetics of Chemical Change in Solution*, The Macmillan Company, New York 1949, Chapter VIII.

Received March 11, 1955.