264. *The Kinetics of the Decomposition of the γ-Bromobutyrate Ion in Neutral and in Alkaline Solution*

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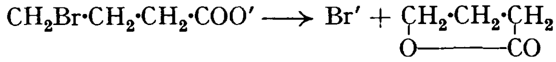
THE kinetics of the reaction



$$CH_2Br\cdot CH_2\cdot CH_2\cdot COO' \longrightarrow Br' + \begin{array}{l} CH_2\cdot CH_2\cdot CH_2 \\ \;| \qquad\qquad\quad | \\ O\text{————}CO \end{array} \quad . \quad . \quad . \quad . \quad (1)$$

which have not hitherto been examined, are peculiarly suitable for study by means of conductivity measurements, and we have made a short survey by this method of the kinetics both of this reaction and of the related hydrolysis in alkaline solution.

γ-Bromobutyric acid was prepared by the series of reactions (see "Organic Syntheses," Coll. Vol. I., p. 425; Marvel and Tannenbaum, *J. Amer. Chem. Soc.*, 1922, **44**, 2645; Marvel and Birkhimer, *ibid.*, 1929, **51**, 260):

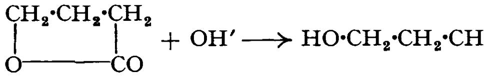
$$C_6H_5{\cdot}OH + Br{\cdot}[CH_2]_3{\cdot}Br \longrightarrow C_6H_5{\cdot}O{\cdot}[CH_2]_3{\cdot}Br \xrightarrow{KCN} C_6H_5{\cdot}O{\cdot}[CH_2]_3{\cdot}CN \xrightarrow{HBr} Br{\cdot}[CH_2]_3{\cdot}CO_2H$$

Since the acid is not stable in aqueous solution, the sodium salt was prepared fresh for each run by evaporating a known volume of a light petroleum solution of the acid and adding an equivalent amount (or any desired excess) of aqueous sodium hydroxide to the residue. The sensitive nature of the conductivity method is well illustrated by the fact that less than 0·8 g. of the acid was sufficient for some 50 runs. The change of conductivity was followed in a cell of 20 c.c. capacity, and the error in the conductivity measurements was of the order of 0·1—0·5% of the total conductivity change according to the concentrations used.

The Decomposition in Neutral Solution.—Measurements were made with the sodium salt in neutral solution at concentrations ranging from 0·003 to 0·0065*N*, and at 25°, 18°, and 0°. The conductivity increased steadily to an asymptotic maximum, and analysis of the results by the Guggenheim method (*Phil. Mag.*, 1926, **2**, 538) gave reproducible and accurately unimolecular constants of $0{\cdot}32_8$, $0{\cdot}10_0$, and $0{\cdot}0041_9$ min.$^{-1}$ (decadic logarithms) respectively. That the reaction involved is a straightforward irreversible lactonisation (1) is confirmed by the observations (*a*) that a colorimetric estimation of the p_H of the solution at the end of all the runs at 25° and 0° showed it to be invariably neutral, (*b*) that the final bromide titre corresponded to the bromine content of the original acid.

The plot of log *k* against $1/T$ is a straight line and leads to an apparent heat of activation of 28,000 cals. When log (*k*/viscosity) is plotted against $1/T$ (see Moelwyn-Hughes, "Kinetics of Reactions in Solution," Chap. VI), the slope gives a value of 32,500 cals. for the heat of activation corrected for the temperature coefficient of the collision frequency. The rate of reaction is more than 10^8 times greater than that corresponding to the number of collisions between the γ-bromobutyrate ion and the solvent with this heat of activation (*idem, ibid.*). This suggests that we are dealing with a truly unimolecular reaction rather than a pseudo-unimolecular reaction involving the solvent, and the observed rate of reaction can be accounted for by postulating at least seven internal degrees of freedom. It seems likely that the rate of lactonisation is determined by the unimolecular ionisation of bromide ion, and that 32,500 cals. corresponds to the activation energy of the ionisation process. Such an ionisation mechanism is not common, but it has been recently used by Hughes (J., 1935, 255; cf. refs. given by Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 604) to interpret the rate of hydrolysis of *tert.*-butyl chloride; the apparent heat of activation which Hughes records (23,060 cals.) may be compared with our own value. If the mechanism we have suggested is correct, it is to be contrasted with that of the acid-catalysed lactonisation of γ-hydroxyvaleric acid (Garrett and Lewis, *J. Amer. Chem. Soc.*, 1923, **45**, 1091).

The Decomposition in Alkaline Solution.—In alkaline solutions containing up to about 1 equiv. of sodium hydroxide, the change of conductivity with time follows a more complicated course. At 25°, the conductivity rises sharply to a maximum, followed by a slow decline to an asymptotic value, at a rate increasing with the hydroxyl-ion concentration; at 0°, the initial peak is not observed, except in solutions containing a relatively small excess of alkali, and the conductivity falls steadily to an asymptotic value. These observations suggest that the process (1) is followed by



$$\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CH_2 \\ | \qquad\qquad | \\ O\text{———}CO \end{array} + OH' \longrightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2' \quad . \quad . \quad . \quad . \quad (2)$$

the absence of the peak at the lower temperature corresponding to the smaller heat of activation (and lower temperature coefficient) of the bimolecular reaction. This hypothesis is borne out by the following further observations: (*a*) the bromide titre of the final solution corresponded to the bromine content of the original acid, (*b*) the irreversibility of the second reaction was established by colorimetric p_H measurements of the final solution, (*c*) a somewhat laborious approximate mathematical analysis of the runs at 25° (for which we are indebted to Mr. W. Barrett) yielded linear plots of certain functions which should be linear on the above reaction scheme. The analysis also yielded values of the two velocity constants which, although subject to various uncertainties, agreed to within 50% with the accurate independent values for reaction (1) derived from the lactonisation experiments in neutral solution and with those for reaction (2) derived from the results described in the next paragraph. The contrast between the stability of the γ-hydroxybutyrate ion in neutral solution and the rapid hydrolysis of the γ-bromobutyrate ion under the same conditions is in accordance with the known polar characteristics of the two substituent groups, since the elimination of a negative ion is involved.

In order to provide further confirmation of the reaction scheme and to evaluate the bimolecular constant more accurately than is possible by analysis of the composite curve, γ-butyrolactone was prepared (from glutaric acid), and its rate of reaction with 1 equiv. of sodium hydroxide was measured in the conductivity apparatus. By a method of analysis which did not involve the initial conductivity reading, the curves were shown to be bimolecular, and yielded velocity constants of 37·2 and 13·8 l./mol.-min. at 25° and 0°, respectively. The conductivity curves for this reaction were identical with those obtained by allowing a solution of sodium γ-bromobutyrate of the same concentration to lactonise completely and then adding 1 equiv. of sodium hydroxide. This identity of the conductivity curves establishes the lactone as a true intermediate compound in the alkaline decomposition, and affords further proof of the simplicity and completeness of the lactonisation reaction in neutral solution; it also provides a useful confirmation of the purity of the acid and lactone used.

The temperature coefficient of the bimolecular reaction between lactone and hydroxyl ion leads to a heat of activation of 6,450 cals. and a "*P*-factor" of 10^{-7}. Such a low value for the *P*-factor of a reaction between an ion and a molecule is unusual but not without precedent (Moelwyn-Hughes, *op. cit.*, p. 218).

SUMMARY.

(1) The decomposition of sodium γ-bromobutyrate in neutral solution and in the presence of sodium hydroxide has been studied by conductivity measurements.

(2) In neutral solution, lactonisation takes place by a unimolecular ionisation mechanism with a heat of activation of 32,500 cals.

(3) In alkaline solution, the lactonisation is followed by a bimolecular reaction of the lactone with hydroxyl ion, having a heat of activation of 6,450 cals. and a *P*-factor of 10^{-7}.

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