164. *A Comparison of the Rates of Hydrolysis of Methyl, Ethyl,* iso*Propyl, and* tert.*-Butyl Bromides in Acetone: Water Catalysis in Such Reactions.*

By William Taylor.

From the observed rates of hydrolysis, *viz.*, $\mathrm{Me} > \mathrm{Et} < \mathrm{Pr}^{\beta} \lll \mathrm{Bu}^{\gamma}$, for this series of bromides in acetone containing " 5% " and " 10% " of water, support is given to a hydrolysis mechanism ($\mathrm{S_m}$) previously proposed (J., 1937, 1965).

Further, the suggestion is made that the catalytic effect of water in such reactions

is due to its dissociating effect on the water already in solution in an organic solvent. A similar explanation is given to interpret the accelerating effect of water on the alcoholysis and acidolysis of alkyl halides.

THE hydrolysis of *tert.*-butyl bromide in acetone containing small concentrations of water is kinetically a second-order reaction. Hence, although the hydrolysis, under these conditions, cannot take place through a unimolecular mechanism, a bimolecular mechanism may be assumed (J., 1937, 1965). Since such solvents are presumably of low ionising power, according to the theory of Hughes and Ingold (J., 1935, 244; see also Hughes, *Trans. Faraday Soc.*, 1938, **34**, 198) a bimolecular mechanism might conceivably have been anticipated. From this viewpoint, then, there is no disagreement between their theory and experiment. However, further experimental evidence given here is widely divergent from what would be expected from their general theory of the hydrolysis of alkyl halides.

If it is accepted that the hydrolysis of *tert.*-butyl bromide under these conditions is bimolecular, then the hydrolyses of methyl, ethyl, and *iso*propyl bromides under the same conditions are most probably also bimolecular. In this case, according to these authors (see also Hughes, *loc. cit.*), the second-order hydrolysis velocity coefficients should be $Me > Et > Pr^{\beta} > Bu^{\gamma}$. The purpose of this investigation was to discover whether or not the coefficients vary in this manner. As shown in Table I they do not, but are in fact $Me > Et < Pr^{\beta} \lll Bu^{\gamma}$.

A similar result (J., 1937, 992), found for the first-order hydrolysis velocity coefficients of the same series of bromides in "60%" and "80%" aqueous ethyl alcohol, has previously been attributed to a break in the reaction mechanism from bimolecular for methyl and ethyl bromides to unimolecular for *iso*propyl and *tert.*-butyl bromides (Bateman and Hughes, J., 1937, 1187). Because this supposed break in reaction mechanism cannot now be considered as the correct interpretation of the similar variation in the hydrolysis rates in "5%" and "10%" aqueous acetone, it is more than possible that the same conclusion holds good for aqueous ethyl alcohol.

An alternative scheme (J., 1937, 1965) is, however, capable of interpreting these results satisfactorily. According to this, all hydrolyses of alkyl halides are bimolecular, and the minimum at Et is held to be due to the decreasing facility of attack of α-carbon by the hydroxyl of the reagent water molecule, together with the concurrently increasing facility of attack of the halogen (of the alkyl halide) by hydrogen of the water, down the series Me, Et, Pr^{β}, Bu^{γ}.

TABLE I.

Values of the second-order velocity coefficients (expressed as l. g.-mol.$^{-1}$ *hr.*$^{-1}$ × 10^5), *for approximately half-reaction, in acetone at* 50°.

G. of H_2O in 100 c.c. of solution.	MeBr.	EtBr.	$Pr^{\beta}Br$.	$Bu^{\gamma}Br$.*
5	9·84	3·02	4·81	5,990
10	16·5	5·22	7·30	18,400

* From J., 1937, 1855.

As noted previously (J., 1937, 1855), water is again seen to have an accelerating effect on its own reaction with an alkyl halide in acetone. Similarly, small concentrations of water accelerate the alcoholysis of benzhydryl chloride in ethyl alcohol (Farinacci and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 2542) and also the acidolysis of α-phenylethyl chloride in acetic acid (Steigman and Hammett, *ibid.*, p. 2539). On the other hand, nitrobenzene retards the alcoholysis of benzhydryl chloride (Farinacci and Hammett, *loc. cit.*). It is now suggested that these catalytic effects are due, not to the ionising effect of water on the alkyl halide (cf. the solvent theory of Hughes and Ingold), but to the dissociating effect of water, and to the associating effect of nitrobenzene, on the hydroxylic reagent R·OH, where R may be H, Alkyl, or Acyl, *i.e.*,

$$(R{\cdot}OH)_n \underset{\substack{(PhNO_2)\\(COMe_2)}}{\overset{(H_2O)}{\rightleftarrows}} nROH$$

The associated form of the reagent is assumed to be relatively unreactive compared with the simple form towards any alkyl halide. On this basis, in computing the second-order velocity coefficients, the active mass of the hydroxylic reagent should be that of the simple molecule, and constant values might then be expected under conditions which vary not too widely.

This interpretation is offered only to account for the catalytic influence of water and of organic solvents such as nitrobenzene and acetone. An explanation of the different rates of elimination of halogen from alkyl halides by different hydroxylic reagents such as water and ethyl alcohol has already been given (J., 1937, 1966) and is distinct from the above.

EXPERIMENTAL.

The methyl, ethyl, and *iso*propyl bromides were materials of constant b. p. The acetone was " AnalaR," purified by the method of Conant and Kirner (*J. Amer. Chem. Soc.*, **1924**, **46**, 246). The procedure in the kinetic experiments was as for *tert.*-butyl bromide (J., 1937, 1855), the temperature again being 50°. Acetone containing 5 g. and 10 g. of water in 100 c.c. of solution at 50° was employed, since no correction due to removal of hydrogen bromide was necessary (see *ibid.*) and also since, the conditions employed for *tert.*-butyl bromide being adhered to, water of this concentration gave measurable rates of development of acidity. The second-order coefficients were calculated from the equation

$$k = [2\cdot303/t(a - b)] \log_{10}[b(a - x)/a(b - x)]$$

t being the time in hours, and a and b the ordinary concentrations (in g.-mol./l.) of water and the alkyl bromide respectively.

Details of representative individual runs are given in Table II, a summary of the results having been given in Table I.

TABLE II.

Methyl bromide.

$a = 5\cdot5556$; $b = 0\cdot2148$.

t	171	268	432	576	746	840	1008	1175	1344
x	0·0300	0·0452	0·0720	0·0914	0·1080	0·1176	0·1302	0·1366	0·1464
$k \times 10^5$	15·9	15·9	17·1	17·5	16·5	17·2	16·9	15·7	15·6

Ethyl bromide.

$a = 5\cdot5556$; $b = 0\cdot1959$.

t	381	572	716	885	980	1148	1315	1485
x	0·0204	0·0294	0·0370	0·0448	0·0496	0·0560	0·0630	0·0666
$k \times 10^5$	5·18	5·11	5·27	5·30	5·38	5·30	5·34	5·06

iso*Propyl bromide.*

$a = 5\cdot5556$; $b = 0\cdot0783$.

t	522	762	1097	1265	1435
x	0·0142	0·0200	0·0296	0·0310	0·0356
$k \times 10^5$	6·90	6·98	7·81	7·18	7·62

In all experiments the dark colour, which was previously observed during the experiments on *tert.*-butyl bromide, developed. From work on olefin formation with these bromides (J., 1937, 1962) it may be assumed that only the substitution reaction (S_m), and no olefin reaction (O_m), occurs.

THE POLYTECHNIC, REGENT STREET, W. 1. [*Received, April 5th*, 1938.]