208. *The Mechanism of Hydrolysis and Alcoholysis of Alkyl Halides : The Reactions of Methyl, Ethyl, and* tert.*-Butyl Bromides with Aqueous Ethyl Alcohol.*

By William Taylor.

According to Hughes and Ingold (J., 1935, 249; see also Fig. 1, *ibid.*, p. 238), for the hydrolysis or alcoholysis of alkyl halides, in the series where Alk = Bu$^{\gamma}$, Pr$^{\beta}$, Et, Me, the velocity of the unimolecular reaction should continuously decrease, and this reaction should in fact be unrealisable or hypothetical for Me and Et. Neither of these deductions, which these authors make from their ionisation theory for such hydrolyses, can be upheld, since it is now found that, not only do both methyl and ethyl bromide suffer the unimolecular reaction in aqueous alcohol, but the velocities are in the order $\mathrm{Bu}^{\gamma} \ggg \mathrm{Me} > \mathrm{Pr}^{\beta} > \mathrm{Et}$ (Table I). As this result is not in agreement with their theory, it casts doubt on their assumption (J., 1935, 251) that the velocities of reaction of hydrogen bromide with the corresponding alkyl acetates in glacial acetic acid, AlkOAc + HBr → AlkBr + HOAc, which are in the order $\mathrm{Bu}^{\gamma} \ggg \mathrm{Pr}^{\beta} \sim \mathrm{Et} < \mathrm{Me}$ (Tronov and Sibgatullin, *Ber.*, 1929, **62**, 2850), are to be interpreted by the transformation of a bimolecular mechanism for Me and Et into a mixed uni- and bi-molecular reaction for Pr$^{\beta}$ and into a unimolecular reaction for Bu$^{\gamma}$. The same may be stated for a similar assumption which Hughes and Ingold make on the basis of Tronov and Ladigina's results (*Ber.*, 1929, **62**, 2844) for the reaction of hydrogen bromide with the corresponding phenolic ethers, AlkOPh + HBr → AlkBr + HOPh, in glacial acetic acid. These observations receive support when compared with the velocities of reaction of hydrogen bromide with the corresponding alcohols, AlkOH + HBr → AlkBr + H_2O. Bennett and Reynolds (J., 1935, 131), using phenol as solvent and the approximate molecular ratios of alcohol : hydrogen bromide : water = 1 : 2 : 10, found $\mathrm{Bu}^{\gamma} \ggg \mathrm{Me} > \mathrm{Pr}^{\beta} > \mathrm{Et}$. Here the mechanism throughout the series is the same (bimolecular) and hence the minimum velocity reached at Et can certainly not be explained by a change of mechanism. The last reaction is the reverse of the hydrolysis of an alkyl bromide, and the two may be supposed to operate through the same, though reversed, mechanisms (Taylor, this vol., p. 344). In this case the bimolecular nature of the esterification reaction would show that the hydrolysis reaction is also truly bimolecular but simulates a unimolecular nature because of the high proportion of one of the reagents, *viz.*, the solvent water. It is, of course, possible that all these five reactions, which exhibit a similar variation of reaction velocity with a change in the nature of the alkyl radical, hydrolysis and alcoholysis being regarded independently, are bimolecular, and in the author's view the minimum at Et in the series AlkX (X = OAc, OPh, OH, Br) is attributable, not to a break from a uni- to a bi-molecular mechanism, but solely to the varying nature of the group Alk. The reagents—water, alcohol, and hydrogen bromide—must be considered as being similar for these purposes and distinct from basic reagents, for which the relative rates are very different, *viz.*, $\mathrm{Me} > \mathrm{Et} > \mathrm{Pr}^{\beta} > \mathrm{Bu}^{\gamma}$ (see, *e.g.*, Hecht, Conrad, and Bruckner, *Z. physikal. Chem.*, 1889, **4**, 288).

Table I.

Values of the first-order velocity coefficients (expressed as min.$^{-1}$ × 10^4) and activation energies (in kg.-cals.).

Solvent (Aqueous EtOH).	MeBr.			EtBr.			Pr$^{\beta}$Br.*			Bu$^{\gamma}$Br.		
	k.			*k.*			*k.*			*k.*		
	55°.	25°.	*E.*	55°.	25°.	*E.*	55°.	25°.	*E.*	25°.	15°.	*E.*
80%	2·87	0·0733	23·7	1·20	0·0303	23·8	1·42	0·0470	(23·16)	198	61·4	20·0
60%	4·98	0·148	22·8	2·40	0·0605	23·8	4·28	0·158	(22·69)	1920	701	17·2

* Values calculated from the equations of Hughes, Ingold, and Shapiro (J., 1936, 225).

Experimental.

Methyl and ethyl bromides were materials of constant b. p. *tert.*-Butyl bromide, prepared by the method of Norris (*Amer. Chem. J.*, 1907, **38**, 641), had b. p. 73—75°/760 mm.

The kinetic experiments were performed with dry, or with 60% and 80% (by vol.) aqueous, ethyl alcohol as solvent media, the alcohol having been dried over and then distilled from lime, followed by refluxing and distillation over calcium. In each experiment 100 c.c. of a solution of the alkyl bromide at the required temperature were taken. The reaction was stopped by adding 10 c.c. of the reaction liquid to benzene (25 c.c.) and water (50 c.c.), and the resulting liquid was titrated with $N/10$-aqueous alkali. The values of the velocity coefficients have been calculated from the equation for a unimolecular reaction: $k = (2{\cdot}303/t) \,.\, \log_{10}a/(a - x)$, a being the concentration of the alkyl bromide in g.-mols./l., and t the time in hours, unless otherwise stated.

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

Methyl bromide.

a = 0·3115; temp. = 55°; solvent, 80% EtOH.

t	4	10	27	67	117	167	331	1008
NaOH c.c.	2·18	5·06	11·75	21·00	26·90	29·40	31·13	30·90
$k \times 10^4$	174	174	175	167	170	172	—	—

Ethyl bromide.

a = 0·1240; temp. = 55°; solvent, 80% EtOH.

t	43	64	91	117	163	422	733
NaOH, c.c.	3·25	4·62	6·03	7·12	8·60	11·80	12·50
$k \times 10^4$	70·7	72·8	73·2	73·0	72·6	71·8	—

Ethyl bromide reacted very slowly indeed with dry ethyl alcohol, and at 55° an " equilibrium " appeared to be established (*i.e.*, titres remained constant) after about 6 weeks, approximately one-sixth of the molecules having apparently reacted. This presumably was due to rate (*b*) equalling rate (*a*) at this, the " equilibrium," concentration.

$$\text{EtBr} + \underset{\text{(solvent)}}{\text{HOEt}} \longrightarrow \text{EtOEt} + \text{HBr} \quad . \; . \; . \; . \quad (a)$$

$$\text{HBr} + \underset{\text{(solvent)}}{\text{HOEt}} \longrightarrow \text{EtBr} + \text{H}_2\text{O} \quad . \; . \; . \; . \; . \quad (b)$$ (see Taylor, this vol., p. 343).

Methyl bromide also appeared to react relatively slowly with the dry solvent, as the following results show, and probably here again reaction (*b*) was responsible.

Methyl bromide.

a = 0·4000; temp. = 55°; solvent, dry EtOH.

t	26	67	117	167	331	655	1008
NaOH, c.c.	3·05	5·28	6·40	7·02	7·98	9·65	10·45

Ethyl bromide.

a = 0·1240; temp. = 55°; solvent, dry EtOH.

t	29	70	243	334	658	1011	1512
NaOH, c.c.	0·40	0·84	1·44	1·60	1·75	2·00	2·00

Details of one run with *tert.*-butyl bromide are :

a = 0·0790; temp. = 25°; solvent, 60% EtOH.

t (mins.)	1·2	2·0	3·0	4·6	6·5	9·0	15·5	30·0
NaOH, c.c.	1·60	2·60	3·55	4·65	5·60	6·45	7·45	7·85
k (min.$^{-1}$)	0·189	0·199	0·199	0·189	0·190	0·189	0·185	—

It may be taken that these are all substitution reactions, and that little or no olefin is formed. This must be true for methyl bromide. Grant and Hinshelwood (J., 1933, 258) found, and Taylor (J., 1935, 1514) confirmed, that, even with alcoholic potash (approx. 0·1N), negligible olefin is obtained from ethyl bromide. Hughes (*J. Amer. Chem. Soc.*, 1935, **57**, 708) showed that no propylene is formed from *iso*propyl bromide under the present experimental conditions; and similarly Hughes (J., 1935, 255) obtained no olefin from *tert.*-butyl chloride in aqueous alcohol even up to 45°.

SUMMARY.

The rates of the first-order reactions of methyl, ethyl, and *tert.*-butyl bromides with aqueous ethyl alcohol have been measured, and a mechanism to interpret the results is discussed.

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