

**392.** *Direct Evidence in Support of a Bimolecular Mechanism for the Hydrolysis of tert.-Alkyl Halides: The Hydrolysis of tert.-Butyl Bromide in Acetone.*

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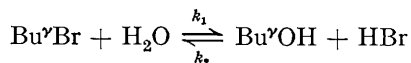
Two items of direct evidence in support of a bimolecular mechanism for the hydrolysis of *tert.*-alkyl halides, obtained by investigating the hydrolysis of *tert.*-butyl bromide in acetone containing small concentrations of water, are: (1) that for the lowest concentrations of water studied, *viz.*, "1%" and "2%," when the effects of these concentrations on the properties of the solvent are probably similar, the second-order velocity coefficients are almost the same; and (2) that for all the concentrations of water studied—"1%" to "10%"—the equilibrium positions calculated, on the assumption of second-order velocity coefficients for both forward and reverse reactions, are almost identical with those observed.

FROM indirect evidence, the author has assumed (this vol., pp. 344, 992) that the mechanism of hydrolysis and alcoholysis of alkyl halides, generally, is bimolecular. This is contrary to the views of Hughes and Ingold (J., 1935, 244), who, according to their ionisation mechanism, regard the hydrolysis of *tert.*-alkyl halides as being unimolecular. If the former view be correct, then, in an inert solvent and for the same molecular concentration of alkyl halide throughout, with small concentrations of water the rate of hydrolysis should be directly proportional to the concentration of water. The object of the present investigation was to find whether this were the case or not, and, in fact, the evidence supports a bimolecular mechanism.

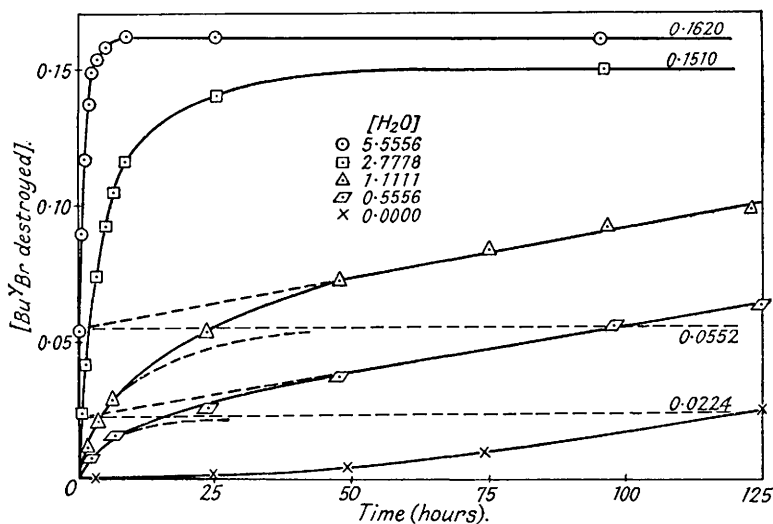
*tert.*-Butyl bromide was chosen as the alkyl halide for two reasons, chiefly because it

was known to be reactive enough to give measurable rates of hydrolysis even with low concentrations of water, and also because the mechanism has been problematical especially in the case of *tert.*-alkyl halides. Acetone was chosen as the solvent since it is non-hydroxylic and could therefore be regarded as being inert to *tert.*-butyl bromide. The considerable difficulties attending the use of this solvent were overcome.

The rates of hydrolysis were measured at 50° with 1, 2, 5, and 10 g. of water in 100 c.c. of acetone solution containing the same concentration of *tert.*-butyl bromide in each case. (These solutions are referred to as containing "1%," "2%," etc., of water.) The plot of the molar concentration of *tert.*-butyl bromide hydrolysed ( $x$ ) against time (see figure) shows the dependence of the rate of hydrolysis upon the concentration of water even at the lowest concentrations. The reaction involved, since water gives little or no olefin with *tert.*-butyl bromide (forthcoming communication), is



and is reversible, but, as can be seen from the figure, a slow reaction persisted beyond the equilibrium position. The increase in acidity produced by this reaction was almost



directly proportional to time, at least for a considerable time interval, and in this respect it was similar to the slow reaction observed by Baker and Nathan (J., 1936, 236) during the reversible reaction between 2 : 4-dinitrobenzyl bromide and benzylpyridinium nitrate in dry acetone. Hence, as in this case, the equilibrium position for any one system was determined by extrapolation of the straight-line portion of the curve back to the  $x$  axis. By determining the rates of the reverse reaction with the same initial concentrations of water as those already stated, and accepting only the earlier values of the second-order rate constants for both reactions, the equilibrium constants  $K = k_1/k_2$  were obtained for the three smallest concentrations of water. From these values of  $K$  the equilibrium positions could be calculated with the aid of Bennett and Mosses' equation (J., 1931, 2957) :

$$n = \frac{K(a+b) + (c+d) - \sqrt{[K(a+b) + c+d]^2 - 4(abK - cd)(K-1)}}{2(K-1)}$$

where  $n$  is the equilibrium value of  $x$ . The values of  $n$  were calculated for the forward reaction only, *i.e.*, when  $c = d = 0$ , since the reverse reaction is retarded with extreme ease by small concentrations of water, as can be seen from the fall in the value of  $k_2$  during any one run and from the great differences in the initial values at the different water concentrations (see also Norris, *Z. physikal. Chem.*, 1927, **130**, 660; *Rec. trav. chim.*, 1929,

48, 885; Levene and Rothen, *J. Biol. Chem.*, 1929, **81**, 359), and therefore no reliance could be placed on the lowest acid concentration reached in this reaction (see below also). The calculated and the observed values of  $n$  are almost identical (Table I) and this constitutes a sound argument for the validity of the assumption made, *viz.*, that *both* reactions are kinetically of the second order. A further piece of direct evidence that the hydrolysis reaction is kinetically of this order is that, with the two lowest water concentrations, where the effect of the water may be taken to alter the general solvent properties of the medium to a similar extent, the second-order values of  $k_1$  are nearly the same. That water has an accelerating solvent effect on the hydrolysis is undoubted from the values of  $k_1$  with the higher concentrations of water (Table I). It might therefore be argued that, in accordance with the ideas of Hughes and Ingold, the increase in  $k_1$  if this were calculated on a first-order basis is due to the effect of the increased ionising powers of the solvent medium on *tert.*-butyl bromide. If so, it would be a coincidence to have such direct proportionality between water concentration and ionising powers as would thereby be held to be exhibited by acetone containing 1% and 2% of water. From this evidence, then, it is contended that the mechanism of hydrolysis of *tert.*-butyl bromide is bimolecular; and the same is held to be true for *tert.*-alkyl halides in general.

TABLE I.

Showing the practical identity of observed and calculated values of  $n$ , the equilibrium position, it being assumed that both reactions are kinetically of the second order.

G. of H <sub>2</sub> O per 100 c.c. of soltn. at 50°.	[Bu <sup>ν</sup> Br] = 0.1620.							
	[H <sub>2</sub> O.]	2nd-Order $k_1$ .	$k_1$ .*	2nd-Order $k_2$ .	$K$ .	$n$ (obs.).	$n$ (calc.).	
1	0.5556	0.0291	0.0337	3.96	0.00735	0.0224	0.0233	
2	1.1111	0.0311	0.0324	1.08	0.0288	0.0552	0.0558	
5	2.7778	0.0599	—	0.0581	1.03	0.1510	0.1500	
10	5.5556	0.184	—	0.000	∞	0.1620	0.1620	

\* Calculated from  $n$  (obs.) and Baker and Nathan's formula (*loc. cit.*) for a bimolecular reversible reaction where the initial concentrations of the reactants are different.

The cause of the continued slow development of acidity in the hydrolysis experiments was the formation of mesityl oxide, phorone, and other unidentified acetone condensation products in the presence of hydrogen bromide. This caused the elimination of water, and hence continued hydrolysis of *tert.*-butyl bromide. The amount of water formed in this way during the reverse reaction was so large as not only greatly to retard the formation of *tert.*-butyl bromide in all except the initial stages, but ultimately even to cause the slow hydrolysis of that already formed, as shown by the rapid decrease in acidity giving place to a slow increase [Table II (b)].

#### EXPERIMENTAL.

The *tert.*-butyl bromide was from the same stock as before (this vol., p. 992); the *tert.*-butyl alcohol had m. p. 25°. "AnalaR" Acetone, dried over sodium sulphate, was first employed, but it was found that, when hydrobromic acid (2 c.c., *d* 1.5) was added to 100 c.c. of this acetone, there was at 50° a gradual disappearance of acidity during approximately 1 hour. An attempt to remove any hydroxylic impurity by refluxing over and distilling from sodium did not overcome this difficulty, nor did purification according to Conant and Kirner (*J. Amer. Chem. Soc.*, 1924, **46**, 246), whose method, however, was applied to "AnalaR" acetone to obtain the solvent used in the kinetic experiments.

In the experiments on the reaction of hydrogen bromide with *tert.*-butyl alcohol, a correction was applied for this removal of acidity in solutions containing initially 1% and 2% of water by performing control experiments with no *tert.*-butyl alcohol present. No correction was necessary with other solutions. The dark brown colour that developed in all solutions, made to examine either forward or reverse reactions, was also observed when hydrogen bromide was present alone in aqueous acetone containing the same proportions of water. Presumably the colour was due to the condensation of the acetone under the influence of hydrogen bromide.

Flasks were calibrated to hold at 20° that volume of acetone which at 50° became 100 c.c., and pipettes were calibrated for 5 or 10 c.c. under the same conditions. In making up the reaction mixtures, measured volumes of water and *tert.*-butyl bromide or of water, hydrobromic

acid (*d* 1.5), and *tert.*-butyl alcohol were put into acetone at 20° in a calibrated flask, and diluted to the mark with acetone. Aliquot portions were immediately pipetted into steamed and dried tubes, which were then put into ice, hermetically sealed, and placed for protection in stout, fairly tightly-fitting tubes in a thermostat at 50°. The temperature of the bath was attained after immersion for 3 minutes, and this was taken as zero time.

To follow the appearance or disappearance of acidity, at suitable times a tube was broken in *ca.* 100 c.c. of absolute ethyl alcohol (previously rendered very faintly alkaline to phenolphthalein) contained in a stoppered bottle. The liquid was titrated with *N*/10-sodium hydroxide or *N*/10-hydrochloric acid. As the reaction liquid became darker, it was more difficult but not impossible to ascertain the end-point.

Since only the initial values of the velocity coefficients  $k_1$  and  $k_2$  could be relied on, owing chiefly to the formation of water caused by the condensation of the acetone, these were sufficiently accurate when calculated from the equation for an irreversible second-order reaction

$$k = [2.303/t(a - b)] \log_{10}[b(a - x)/a(b - x)]$$

*t* being the time in hours, and *a* and *b* the concentrations (in g.-mols./l.) of water and *tert.*-butyl bromide respectively in the forward reaction, and of *tert.*-butyl alcohol and hydrogen bromide respectively in the reverse reaction. However, for the forward reaction in acetone containing 1% and 2% of water, Baker and Nathan's equation (*loc. cit.*) for a bimolecular reversible reaction was also applied in conjunction with the observed values of *n* for the equilibrium position (see Table II).

TABLE II.

(a) *Details of experiments on the forward reaction.*

Expt. 1; <i>a</i> = 5.5556.						Expt. 2; <i>a</i> = 2.7778.					
<i>t.</i>	<i>x.</i>	$k_1$ .	<i>t.</i>	<i>x.</i>	$k_1$ .	<i>t.</i>	<i>x.</i>	$k_1$ .	<i>t.</i>	<i>x.</i>	$k_1$ .
0.40	0.0530	0.180	2.90	0.1528	0.181	0.95	0.0236	0.0599	6.6	0.1060	0.0593
0.85	0.0902	0.174	4.57	0.1580	—	1.90	0.0426	0.0583	8.25	0.1170	0.0587
1.33	0.1180	0.179	7.78	0.1625	—	3.63	0.0740	0.0614	25	0.1410	(0.0298)
1.78	0.1378	0.195	25	0.1620	—	5.02	0.0936	0.0630	96.5	0.1510	—
2.37	0.1490	0.195	96	0.1620	—						

Expt. 3; <i>a</i> = 1.1111.						Expt. 4; <i>a</i> = 0.5556.					
<i>t.</i>	<i>x.</i>	$k_1$ .	$k_1$ .*	<i>t.</i>	<i>x.</i>	<i>t.</i>	<i>x.</i>	$k_1$ .	$k_1$ .*	<i>t.</i>	<i>x.</i>
2.0	0.0112	0.0326	0.0327	75	0.0850	3.0	0.0080	0.0299	0.0318	99	0.0562
4.0	0.0216	0.0326	0.0338	98	0.0960	7.0	0.0166	0.0282	0.0357	120	0.0640
6.6	0.0298	0.0281	0.0306	119	0.1000	24	0.0256	(0.0132)	—	175	0.0856
24	0.0540	(0.0156)	—	286	0.1290	48	0.0380	(0.0104)	—	287	0.1074
48	0.0742	(0.0124)	—								

(b) *Details of experiments on the reverse reaction.*

Expt. 5; <i>a</i> = 0.2077, <i>b</i> = 0.1730, [H <sub>2</sub> O] = 5.5556.					Expt. 6; <i>a</i> = 0.2077, <i>b</i> = 0.1730, [H <sub>2</sub> O] = 2.7778.				
<i>t.</i>	<i>b</i> - <i>x.</i>	<i>t.</i>	<i>b</i> - <i>x.</i>	$k_2$ .	<i>t.</i>	<i>b</i> - <i>x.</i>	$k_2$ .	<i>t.</i>	<i>b</i> - <i>x.</i>
0.20	0.1725	25.0	0.1735	—	0.20	0.1730	—	24	0.1610
0.50	0.1730	241	0.1730	—	0.80	0.1710	0.0664	51	0.1610
7.0	0.1730	624	0.1735	—	6.4	0.1620	0.0498	240	0.1630

Expt. 7; <i>a</i> = 0.2077, <i>b</i> = 0.1730, [H <sub>2</sub> O] = 1.1111.					Expt. 8; <i>a</i> = 0.1038, <i>b</i> = 0.0865, [H <sub>2</sub> O] = 0.5556.				
<i>t.</i>	<i>b</i> - <i>x.</i>	$\delta x$ .*	<i>b</i> - <i>x</i> (corr.).	$k_2$ .	<i>t.</i>	<i>b</i> - <i>x.</i>	$\delta x$ .*	<i>b</i> - <i>x</i> (corr.).	$k_2$ .
0.1	0.1672	0.0015	0.1687	1.13	0.1	0.0816	0.0014	0.0830	3.99
0.2	0.1616	0.0034	0.1650	1.13	0.18	0.0774	0.0032	0.0806	3.92
0.33	0.1556	0.0056	0.1612	1.03	0.33	0.0740	0.0047	0.0787	(2.86)
0.67	0.1420	0.0087	0.1507	1.04	0.67	0.0672	0.0076	0.0748	(2.23)
1.33	0.1268	0.0120	0.1388	(0.868)	1.17	0.0574	0.0100	0.0674	(2.28)
3.33	0.1022	—	0.1142	(0.712)	3.0	0.0436	0.0115	0.0551	(1.74)
5.25	0.0934	—	0.1054	(0.558)	6.7	0.0364	—	0.0479	(1.09)
26	0.0850	—	0.0970	(0.140)	27	0.0254	—	0.0369	(0.43)
51	0.0954	—	0.1074	—	52	0.0300	—	0.0415	—
215	0.1290	—	0.1410	—	216	0.0510	—	0.0625	—

\*  $\delta x$  is the correction applied for the removal of acidity by acetone itself, containing initially hydrogen bromide and water of the given concentrations.

An experiment with *tert.*-butyl bromide and dry acetone recorded below appears to indicate that even very small traces of moisture, possibly in the air in the sealed tubes, caused elimination

of hydrogen bromide. (Alternatively, even dry acetone itself may react to this slight extent with *tert.*-butyl bromide.) This in turn caused condensation of the acetone, and hence the formation of water followed by continued hydrolysis of the alkyl bromide. There was thus an "induction period" in the formation of acid (see fig.), followed, after approximately 3 days, by a rate which was almost directly proportional to time.

			$a = 0.0000; b = 0.1620$					
$t$ .....	0	6	24	49	74	125	262	383
$10^4 x$ .....	—	—	20	60	100	260	680	1000

Attempts to ascertain the proportions of olefin formed from *tert.*-butyl bromide by the procedure adopted previously (this vol., p. 344) failed, since, with the lower concentrations of water, over 100% olefin was indicated. This was undoubtedly due to the formation of unsaturated compounds such as mesityl oxide.

*Isolation and Identification of Mesityl Oxide and Phorone.*—(a) *Dry hydrogen bromide and acetone.* Dry hydrogen bromide was passed through ice-cold acetone until the acidity was approximately  $N$ . The liquid (100 c.c.) was maintained at  $50^\circ$  for 48 hours; water was added, and the liquid extracted with ether. Distillation gave fractions: (1) b. p.  $120$ — $150^\circ$  (3.7 g.), (2) b. p.  $150$ — $195^\circ$  (1.5 g.). About 4 g. of deep brown tarry liquid remained.

(b) *tert.-Butyl alcohol, hydrogen bromide, and acetone.* The alcohol (4.5 g.) in acetone (150 c.c.), containing hydrogen bromide of the same concentration as in (a), was maintained at  $50^\circ$  for 48 hours, then shaken with water to destroy all butyl bromide, extracted with ether, and distilled; three fractions were obtained: (1a) b. p.  $60$ — $120^\circ$  (4.1 g.), (1) b. p.  $120$ — $150^\circ$  (5.1 g.), (2) b. p.  $150$ — $195^\circ$  (1.1 g.). Some dark tarry liquid (3.6 g.) remained.

(c) *tert.-Butyl bromide, water, and acetone.* *tert.*-Butyl bromide (6 g.) and water (1 g.) in acetone (100 c.c.) were treated as in (b). The fractions were: (1a) b. p.  $60$ — $120^\circ$  (1.5 g.), (1) b. p.  $120$ — $150^\circ$  (1.6 g.), (2) b. p.  $150$ — $200^\circ$  (0.6 g.), and undistilled tarry liquid (2.0 g.) remained.

(d) *Examination of fractions from (a), (b), and (c).* (i) In each case a few drops of fraction (1) in ethyl-alcoholic solution yielded considerable amounts of the carmine-coloured 2:4-dinitrophenylhydrazone of mesityl oxide (m. p. and mixed m. p. with authentic specimen).

(ii) Phorone was identified through its tetrabromide (m. p. and mixed m. p. with authentic specimen), isolated according to Claisen (*Annalen*, 1876, **180**, 12), and was present in small quantities in all fractions (2). It was necessary to leave the brominated mixture at room temperatures for 2 weeks to allow the tetrabromide to crystallise from the preponderating amount of oil (presumably mesityl oxide dibromide) also present.

(iii) Attempted oxidation of fractions (2) with alkaline permanganate failed to afford any trimesic acid, so mesitylene was absent.