176. *Mechanism of Substitution at a Saturated Carbon Atom. Part XI.** *Hydrolysis of* tert.-*Butyl Bromide in Acidic Moist Acetone.*

By Leslie C. Bateman, Kenneth A. Cooper, and Edward D. Hughes.

The evidence recorded by Taylor in support of a bimolecular mechanism for the hydrolysis of *tert.*-butyl bromide in moist acetone is shown to be worthless.

Taylor assumes that the halide is involved simply in a reversible reaction

$$\text{Bu}^\gamma\text{Br} + \text{H}_2\text{O} \rightleftharpoons \text{Bu}^\gamma\text{OH} + \text{HBr},$$

and he adduces " two items of direct evidence " in favour of a bimolecular hydrolysis. One is based on a claimed exact agreement between the " observed " equilibrium concentrations and those " calculated " from measured rates on the assumption that the forward and the reverse reaction are of the second order. The other is based on the approximate identity of the recorded second-order rate constants for the hydrolysis in acetone containing 1 and 2 vols. % of water.

Regarding the first " item of evidence," it is now shown that the represented equilibrium does not exist under the conditions of Taylor's experiments in moist acetone. His method of " observation " is analysed and found to be illusory. Furthermore, rates which form an essential part of the basis of the " calculation " of equilibrium compositions are shown to have no quantitative meaning. Finally, the method of calculation which produces the perfect agreement out of the imperfect experimental material is shown to be an incorrect method for Taylor's stated purpose.

As to Taylor's second " item of evidence," it is pointed out that this also is valueless, since, on making small additions of a " rapid " to a " slow " (or inactive) solvent, initial proportionality between the specific rate and the concentration of the minor solvent constituent is to be expected on the unimolecular mechanism, *i.e.*, when there is *no* stoicheiometric intervention by water in the rate-measured process.

We have now to record a criticism and revision of a group of Taylor's experiments (paper 5; references, this vol., p. 900) which he has repeatedly cited (cf., *e.g.*, papers 6, 8 and 9) as evidence that the hydrolysis of *tert.*-butyl bromide in moist acetone is bimolecular, and that by implication the hydrolyses of all alkyl halides in aqueous solvents are likewise bimolecular. He employs two methods.

(1) *Taylor's First Method.*

This consists of three steps, of which the first was to follow the development of acid from *tert.*-butyl bromide in moist acetone. It is assumed that the halide is involved simply in the reversible reaction

$$\underset{(a)}{\text{Bu}^\gamma\text{Br}} + \underset{(b)}{\text{H}_2\text{O}} \underset{k_2''}{\overset{k_2'}{\rightleftharpoons}} \underset{(c)}{\text{Bu}^\gamma\text{OH}} + \underset{(d)}{\text{HBr}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

and that different, determinable equilibria are reached when the solvent acetone contains different proportions, 1, 2 or more vols. %, of water.† Having " determined " these equilibria, his next step was to measure the initial rates of the forward and the reverse reaction, and to express these rates as second-order constants, *i.e.*, first order with respect to each of the two reactants shown on either side of equation (1). The third step was to calculate the concentration of *tert.*-butyl bromide at equilibrium from these initial rates by means of that mass-law formula which assumes the reaction each way to be of the second order, and to compare the calculated equilibrium concentrations with the " observed " values.

An extremely accurate agreement was exhibited (mean deviation, 1·5%), and it was contended that " this constitutes a sound argument for the validity of the assumption made, *viz.*, that *both* reactions are kinetically of the second order."

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* The serial number was inadvertently omitted from the title of Part X (J., 1938, 881).

† If comparison be made with Taylor's paper, it should be noted that we use k_2', k_2'', K_{22} and x_∞ where he employs k_1, k_2, K and n respectively. In our notation the subscripts to k and K indicate the assumed reaction order; one dash denotes the forward reaction, two the back reaction.

FIG. 1.

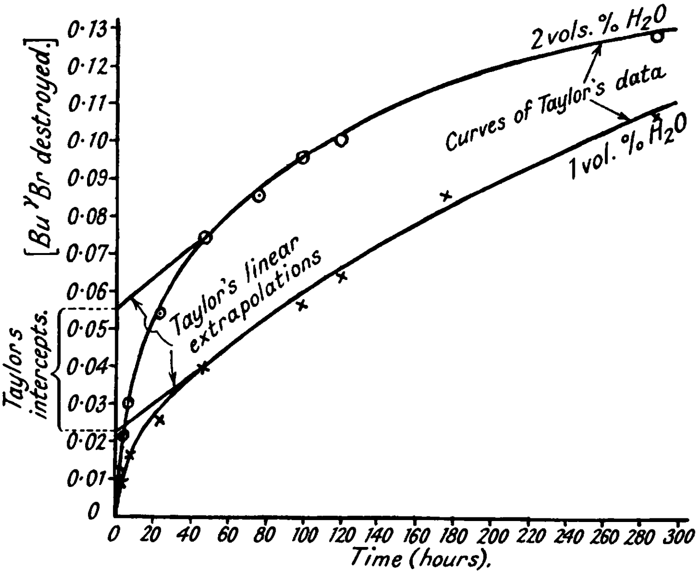
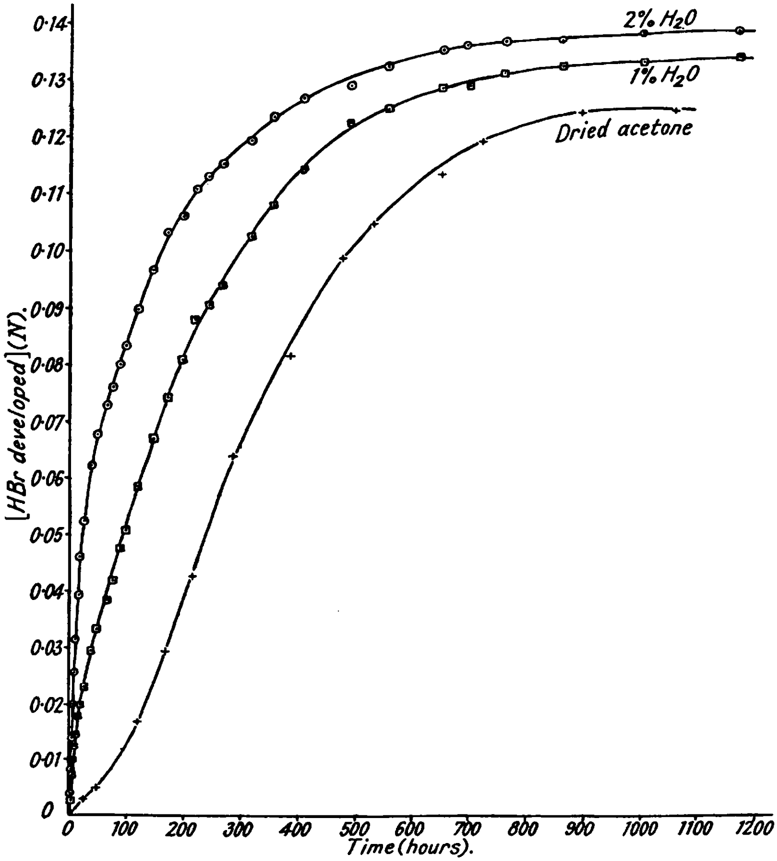

0·13
0·12
0·11
0·10
0·09
0·08
0·07
0·06
0·05
0·04
0·03
0·02
0·01
0
[Bu^γBr destroyed.]
Taylor's intercepts.
2 vols. % H₂O
Curves of Taylor's data
1 vol. % H₂O
Taylor's linear extrapolations
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300
Time (hours).

FIG. 2.


0·14
0·13
0·12
0·11
0·10
0·09
0·08
0·07
0·06
0·05
0·04
0·03
0·02
0·01
0
[HBr developed](N).
2% H₂O
1% H₂O
Dried acetone
0 100 200 300 400 500 600 700 800 900 1000 1100 1200
Time (hours).

We will consider the first step, *viz.*, the experimental determination of the supposed equilibria. Taylor found, and we confirm, that when hydrogen bromide is liberated in acetone containing *small* percentages (*e.g.*, 1 or 2%) of water (or in dried acetone) the solution turns brown, and, if *tert.*-butyl bromide is present, the further liberation of hydrogen bromide goes on continuously.* Taylor's explanation of this is probably correct (though insufficient—see below), *viz.*, that the self-condensation of acetone under the influence of hydrogen bromide liberates water, which then contributes to the further hydrolysis of the *tert.*-butyl bromide. However, it means that the supposed equilibria corresponding to equation (1) cannot be observed directly. Accordingly, Taylor " observed " them by selecting from the reaction–time curves parts which he regarded as rectilinear, and producing these backwards to cut off from the composition axis intercepts which he claimed to represent the " equilibrium " compositions.

In Fig. 1 we have replotted Taylor's own data for acetone containing 1 and 2 vols. % of water, and have reproduced his linear extrapolation. From this diagram alone it would appear that his method of " observing " the " equilibrium " compositions for these solvents is arbitrary. It would, of course, be possible to assess the equilibrium compositions with some degree of accuracy if the disturbance due to the solvent reaction were slow in comparison with the hydrolysis. Taylor states that " a slow reaction persisted beyond the equilibrium position," but a glance at the slopes of his " straight lines " for 1 and 2% of water, in relation to the complete curves for these solvents (*loc. cit.*, figure p. 1854; cf. Fig. 1), shows that this is not a just description.

Our reaction–time curves for the two solvents of main significance in Taylor's argument, those with 1 and 2% of water, are shown in Fig. 2, together with our curve for dried acetone. The temperature, 50·0°, is the same as that employed by Taylor. We took more readings than he records, and followed the reactions further. It will be seen that no part of these curves is free from curvature. One can, of course, draw *tangents*, but the slopes are arbitrary within wide limits, and it is certainly not possible to fix intercepts with anything like the accuracy of the claimed agreement with the calculated values.† ‡

In any case the whole procedure is meaningless, because there are other reasons, besides the decomposition of the acetone, why the equilibrium represented in equation (1) does not exist under the conditions of these experiments; at least three of the four indicated reactants are otherwise occupied. The first of these is *tert.*-butyl bromide. Taylor tried to detect *iso*butylene by a method which could not be successful. He therefore decided that, since the amount of *iso*butylene formed in water is small, the amount produced in wet acetone would be small enough to be neglected. But we find that, in acetone with 2 vols. % of water, 55—60% of the product from *tert.*-butyl bromide is *iso*butylene. Probably with only 1% of water the proportion is higher (this vol., p. 901). The other two reactants which cannot be concerned in reaction (1) alone are water and hydrogen bromide. These will never remain as such in presence of each other in moist acetone, but will give H_3O^+ and Br^- to an extent varying with both the instantaneous acidity and the water content of the medium.

Furthermore, in Taylor's procedure it is assumed that all the bromine is present either as *tert.*-butyl bromide or as hydrogen bromide [cf. equation (1)]. Independently of our foregoing remarks about the condition of hydrogen bromide, this assumption is demonstrably incorrect for acetone containing 1 and 2 vols. % of water. In the experimental section we describe a method suitable for the estimation of both of the halides in question. Briefly, it involves the complete hydrolysis of the unchanged *tert.*-butyl bromide, and its

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* This disturbance does not apply to the solvent containing 5 vols. % of water, or to the still more aqueous solvents used by us in some of the following papers.

† If comparisons of rates be made with Taylor's data, it should be noted that our solvent and his were of slightly different composition (cf. experimental section).

‡ A *local* and *partial* flattening of the curves for 1 and 2 vols. % of water is to be expected, because the acetone reaction must be autocatalytic and there would be some stage at which the upward curvature of its time-curve would tend to compensate the steady downward curvature which would be observed in the absence of this disturbance. If the autocatalytic contribution to the curvature were strong enough, the curves would exhibit a point of inflexion, as will be illustrated in the next paper.

subsequent estimation as hydrogen bromide, after the concentration of the acid already formed in the reaction has been determined. In the initial stages of the reactions the total halide, which can be estimated by this procedure, is in quantitative agreement with the amount of *tert.*-butyl bromide originally introduced, but when the solvent decomposition becomes obvious the combined estimate ($\mathrm{Bu^{\gamma}Br} + \mathrm{HBr}$) begins to decrease.

We pass now to the consideration of Taylor's second step, *viz.*, the attempted determination of rate constants for the two individual reactions of equation (1), as material for the calculation of the proportion of reactants at " equilibrium." This calculation was made for three solvents, *viz.*, acetone containing 1, 2 and 5 vols. % of water. The six necessary rate constants are given to three significant figures, but they are deduced from titre differences of the order of 1 c.c. One constant, quoted as 0·0581, comes from just two titrations, one of which can be calculated to be either 0·2 c.c. or 0·1 c.c., and the other either 1·1 c.c. or 0·55 c.c. (there is an ambiguity in the experimental description). The values of the constant, as calculated from these readings individually, are 0·0664 and 0·0498; and Taylor takes the average (0·0581). In another case the constant is again based on two titrations, of which the larger is either 1·6 c.c. or 0·8 c.c. In another it is also based on two titre differences, the larger being either 0·9 c.c. or 0·45 c.c., and " corrections " of up to 35% are applied to allow for the destruction of acidity by the acetone itself. At least one of the two " constants " employed in the calculation of the equilibrium composition for any one medium can be criticised similarly. (A further constant was obtained for acetone with 10 vols. % of water, but its companion was too small to measure.) The claimed precise agreement of the calculated and the observed compositions is therefore even more remarkable than our previous comments (on the method of observation) indicated.

Finally, we shall consider Taylor's third step, *viz.*, his method of calculation. As stated previously, Taylor expressed his rates as second-order constants, and used the formula appropriate to a balanced reaction of the second order in both directions, *viz.*,

$$x_{\infty} = \frac{K_{22}(a+b) + (c+d) - \sqrt{[K_{22}(a+b) + (c+d)]^2 - 4(abK_{22} - cd)(K_{22} - 1)}}{2(K_{22} - 1)} \quad (2)$$

where x_{∞} is the concentration representing the extent of the forward reaction at equilibrium, a, b, c and d are initial concentrations applying as indicated under equation (1), and $K_{22} = k_2'/k_2''$. Taylor claimed that the great success of equation (2) justified the assumption of a second-order forward reaction.

Now it does not require an algebraic analysis of equation (2) to see that, even if none of our previous criticisms was justified, *i.e.*, if the reactions of equation (1) were the only ones, if the compositions at equilibrium had really been measured, and if the individual rate constants had really been determined with precision, an agreement between observed and calculated compositions at equilibrium would owe nothing whatever to the special form of equation (2), and, in particular, nothing to the assumed second-order character of the forward reaction. For, in a pair of balanced reactions, each individual rate constant is essentially an expression of behaviour of the system in the *early* stages of reaction, and therefore an equation such as (2), which involves these constants, although it will be *valid*, will only be *critical* provided *no reagent concentration is buffered in those early stages.* But in all Taylor's measurements of the rate constants for the forward reaction the water concentration was strongly buffered, not only over the range for which the constants were determined, but also over any range for which they might individually have expressed the behaviour of the system, had all the various disturbances been absent. In the most favourable case the absolute value of the water concentration was *ca.* 20 times larger than its variation, and this factor was generally much greater. In order to illustrate the principle here involved, we have calculated x_{∞} from Taylor's data on the assumption that the forward reaction is of the first order, whilst the back reaction remains of the second order. For this purpose we re-express his second-order constants, k_2', as first-order constants k_1' (as we may do because of the buffered water concentrations), retain his second-order constants k_2'', and use formula (3) wherein $K_{12} = k_1'/k_2''$:

$$x_{\infty} = \tfrac{1}{2}\sqrt{(K_{12} + c + d)^2 + 4(K_{12}a - cd)} - \tfrac{1}{2}(K_{12} + c + d) \quad . \quad . \quad . \quad (3)$$

Taylor gives a table " showing the practical identity of observed and calculated values of the equilibrium position, it being assumed that both reactions are kinetically of the second order." We copy his figures in Table I and add another column showing the value of x_∞ as calculated by equation (3), which assumes that the forward reaction is kinetically of the first order.

TABLE I.

From Taylor's Table.						Eqn. (3).
Vols. % H_2O.	$[H_2O]$.	k_2'.	k_2''.	x_∞ (obs.).	x_∞ (calc.).	x_∞ (calc.).
1	0·5556	0·0291	3·96	0·0224	0·0233	0·0237
2	1·1111	0·0311	1·08	0·0552	0·0558	0·0577
5	2·7778	0·0599	0·0581	0·1510	0·1500	0·1537
10	5·5556	0·184	0·000	0·1620	0·1620	(0·1620)*

* This calculation and Taylor's corresponding one are trivial because there is no measurable back-reaction : the figure 0·1620 simply represents the amount of *tert.*-butyl bromide taken.

In judging the agreement it must be remembered that, in general,* neither the " observed " values based on Taylor's linear extrapolation, nor his experimental data underlying either set of calculated figures have any quantitative value. Thus it is far from our intention to claim that the agreement of an ill-founded application of equation (3) with " observed " values, which also agree excellently with an equally ill-founded application of equation (2), has any mechanistic consequences.

(2) *Taylor's Second Method.*

This may be described in Taylor's own words.† " A further piece of direct evidence that the hydrolysis reaction is kinetically of this [the second] order is that, with the two lowest water concentrations, *when 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_2' are nearly the same," *i.e.*, the fraction of halide initially decomposed per second is about twice as great with 2% as with 1% of water. Taylor continues : " That water has an accelerating solvent effect on the hydrolysis is undoubted from the values of k_2' 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 of k' if this was calculated on a first-order basis (k_1') 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." (Two passages are here italicised by us for convenience in later reference.)

Consider for simplicity a reaction in which the solvent plays no stoicheiometric part. Let there be two fully miscible solvent constituents A and B such that the rate in pure B is, say, 10,000 times greater than the rate in pure A. For intermediate solvent compositions the rate will be given by some smooth curve : to make the illustration very simple, suppose that the curve is a straight line. Then, if we add 1% of B to A, we shall increase the rate from k_1' to $101k_1'$. If we add 2%, the value will be $201k_1'$. In fact we shall get practical proportionality. Now pass to the more general case in which the rate–composition curve is not straight. We can then draw a tangent at the A-end. Suppose that this cuts the B-axis at, say, $20{,}000k_1'$, or $5000k_1'$ (depending on whether the curve is concave or convex to the composition axis). Obviously we shall still get initial proportionality, though with a different proportionality constant. As long as one makes sufficiently small additions of the much more active to the much less active solvent, proportionality is inevitable. It is

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* The observed value of x_∞ in acetone containing 5 vols. % of water may be reasonably accurate.

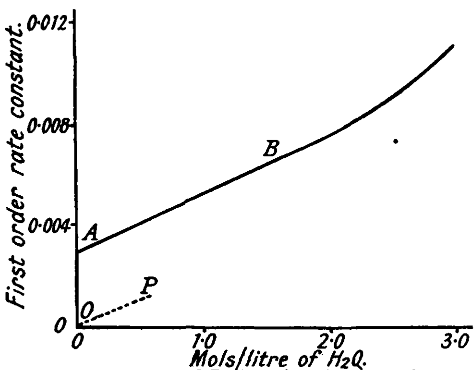
† Except that, for clearness, we keep to our own k-notation.

‡ See our Table I.

clear that this holds also if the solvent does take stoicheiometric part in the reaction as a whole, but does not take such a part in the rate-determining stage.*

An excellent illustration of this behaviour was recently given by Farinacci and Hammett (*J. Amer. Chem. Soc.*, 1937, **59**, 2542) in the example of the reaction of benzhydryl chloride with ethyl alcohol containing various percentages of water. There was a small first-order rate in pure ethyl alcohol, and the rate rose sharply and (at first) linearly with the proportion of added water (Fig. 3). The naïve argument would be that the excess rate, *i.e.*, the excess over the part *OA* due to alcohol (the concentration of which is sensibly constant throughout the solvent range) represents the second-order reaction $CHPh_2Cl + H_2O \longrightarrow CHPh_2{\cdot}OH + HCl$. But Farinacci and Hammett showed that this was not so : the main function of the water is not to produce benzhydrol, but to accelerate the formation of benzhydryl ethyl ether. It is an effect due to what Taylor calls "general solvent properties," and, in accordance with the preceding paragraph, must (and does) start linearly. Of course, if the alcohol had been acetone, the curve *AB* would have started not from *A* but from *O* (*e.g.*, curve *OP*), and we should have had proportionality (and, naturally, a formation only of benzhydrol).

Fig. 3.



(Data of Farinacci and Hammett)

Referring to the italicised passages, we see there is no justification for the statement that two percentages of water, one twice the other, will alter solvent properties to a similar extent. Furthermore, the " coincidence " of proportionality in the initial stages of water addition is expected on Hughes and Ingold's theory.

Taylor's research seems to have been designed in order to counter one of ours, wherein we added 1, 2, 5 and 10% of water to formic acid and obtained substantially identical first-order rates for the hydrolysis of *tert.*-butyl chloride, *i.e.*, the specific rate was independent of the water concentration. Here, however, a different situation arises : the whole point of the choice of formic acid was that its activity as solvent should at least *not be very small* compared with that of water (how much greater it might be does not matter). Again, taking the figure 10,000 to denote the solvent activity of water, that of formic acid might be represented by, say, 2000, or 50,000 or 500,000. Using, in illustration, the figure 2000 for formic acid, we see that 1% of water should change this to 2100, 2% to 2200, and so on, if the rate–composition curve is rectilinear throughout. Initially, the curve must, as we have seen, be rectilinear. When this relationship begins to fail, it is impossible to predict, *a priori*, what form to assume, but general experience indicates that, for the type of reaction under discussion, the departure is as shown in Fig. 3, *i.e.*, the effect of admixture is smaller in the initial stages than later. For small percentages of water, a serious departure from approximate constancy in the rate, in so far as this is determined by the solvent effect, is, therefore, very improbable. A similar result follows if we take the figure 500,000 for formic acid.

The slope of the rectilinear portion of any such curve will depend jointly on the solvent effect and on the kinetic order (first or second) of the constants chosen to express the rates. If the solvent effect alone should give a *horizontal*, rectilinear curve, then that reaction order will be correctly chosen whose constants actually give a horizontal curve. In our case this order was first. Our purpose here is simply to make it clear that it is only in the case which Taylor chose, *viz.*, the progressive addition of a much more active solvent to a much less active one, that the naïve conclusion derived from the apparent reaction order fails; we shall deal in the next paper but two with Taylor's suggestion that the reaction in formic acid consists in the formation and hydrolysis of *tert.*-butyl formate.

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* Adapting an old type of nomenclature, a unimolecular reaction, influenced by solvent in this way, might be called " pseudo-bimolecular."

Reverting to the acetone solvents, the conclusion of this paper is simply that Taylor's evidence of mechanism is worthless. In later papers we shall present evidence of another type, leading to a somewhat detailed picture of what happens in aqueous hydrolysis.

EXPERIMENTAL.

Materials.—*tert.*-Butyl bromide, prepared as previously described (Cooper and Hughes, J., 1937, 1183), was dried over phosphoric oxide and fractionated, b. p. 72·8—73·8°/756 mm. Acetone was purified by the method of Conant and Kirner (*J. Amer. Chem. Soc.*, 1924, **46**, 246)—the method also employed by Taylor.

Rate Measurements.—A suitable quantity of *tert.*-butyl bromide was dissolved either in pure acetone or in acetone containing a weighed amount of water, and the solution was made up to 250 c.c. at 20°. Portions of 5 c.c. were enclosed in sealed tubes, which were immersed in a thermostat at 50·0° ± 0·02° for known times, and then broken under 100 c.c. of cold acetone to stop the reaction. The acidity was titrated against 0·0406N-sodium hydroxide with lacmoid as indicator. In a number of cases the neutral acetone solution was then diluted with an equal volume of water to complete the hydrolysis of the unchanged *tert.*-butyl bromide, and the additional acidity was determined as before. In order to eliminate error due to reaction before the mixtures had reached the temperature of the thermostat, an ' initial ' estimation was made on a sample which had been shaken in the thermostat for 5 minutes. The samples used for the other estimations were similarly treated for 5 minutes, the end of which period was taken as the zero of time. The results are in Table II, where t is the time in hours, and x and y the concentrations of hydrogen bromide and unchanged *tert.*-butyl bromide, respectively, in g.-mols./l.; the concentrations recorded are not corrected for expansion.

TABLE II.

Expt. 1; $[\mathrm{Bu}^{\gamma}\mathrm{Br}] = 0{\cdot}1496\mathrm{N}$, $[\mathrm{H_2O}] = 0$.

t	23·5	47	119	166	213	285	383	478	530	645
x	0·0029	0·0048	0·0166	0·0295	0·0427	0·0639	0·0816	0·0987	0·1047	0·1135
t	719	891	1054							
x	0·1193	0·1241	0·1249							

Expt. 2; $[\mathrm{Bu}^{\gamma}\mathrm{Br}] = 0{\cdot}1512\mathrm{N}$, $[\mathrm{H_2O}] = 0{\cdot}5386\mathrm{N}$.

t	0	1·25	3·6	5·25	7·25	9·5	14·0	18·0	24·25	38·0
x	0	0·0026	0·0071	0·0097	0·0122	0·0144	0·0177	0·0199	0·0230	0·0295
$x+y$	0·1512	—	0·1492	0·1481	0·1474	—	0·1461	—	0·1446	0·1420
t	48·25	62·5	72·6	87·4	97·5	119·4	144·3	167·9	192·8	217
x	0·0335	0·0386	0·0420	0·0476	0·0509	0·0589	0·0670	0·0744	0·0810	0·0880
$x+y$	—	—	—	0·1398	0·1384	—	—	—	—	—
t	240	264	315	354	406	489	552	650	688	758
x	0·0904	0·0942	0·1025	0·1080	0·1142	0·1224	0·1247	0·1285	0·1287	0·1312
t	863	1003	1168	1384						
x	0·1326	0·1330	0·1342	0·1345						

Expt. 3; $[\mathrm{Bu}^{\gamma}\mathrm{Br}] = 0{\cdot}1527\mathrm{N}$, $[\mathrm{H_2O}] = 1{\cdot}0808\mathrm{N}$.

t	0	1·0	2·0	3·4	5·0	7·0	9·25	14·0	18·0	24·0
x	0	0·0037	0·0083	0·0141	0·0200	0·0258	0·0316	0·0394	0·0459	0·0526
$x+y$	0·1527	—	0·1516	0·1519	—	—	0·1519	0·1514	—	—
t	38·0	48	62·5	72·4	87·4	97·3	119·4	144·3	167·8	192·4
x	0·0620	0·0677	0·0729	0·0759	0·0802	0·0832	0·0896	0·0966	0·1032	0·1058
$x+y$	0·1510	0·1495	0·1485	0·1493	0·1489	0·1480	0·1465	—	—	—
t	217	240	264	315	354	406	489	552	650	688
x	0·1104	0·1131	0·1150	0·1194	0·1231	0·1268	0·1287	0·1324	0·1352	0·1364
t	758	863	1003	1168	1384					
x	0·1368	0·1370	0·1386	0·1390	0·1391					

Estimation of iso*Butylene.*—The extraction method of olefin estimation cannot possibly succeed in the presence of acetone and its decomposition products (cf. Taylor, *loc. cit.*). We, therefore, adopted an aspiration technique which, essentially, was carried out as previously described (cf. this vol., p. 901). Two solvents were investigated, *viz.*, acetone containing 2 and 10 vols. % of water. The results and experimental details of special importance are summarised on p. 920.

(a) 2% *Aqueous acetone.* The reaction mixture, made up as described for the kinetic experiments, was contained in a flask kept at 50°, and the olefin was aspirated through a vertical water condenser and a trap at 0° and finally absorbed in a dilute solution of bromine in carbon tetrachloride. In order to minimise disturbances due to the decomposition of the medium the estimation was carried out after the completion of about 10% of reaction. A blank experiment with the medium, *tert.*-butyl alcohol and hydrogen bromide (quantities corresponding to 10% reaction) was similarly performed, and a correction was accordingly applied to the results of the olefin estimations; 55—60% of olefin formation was thus indicated. We do not claim great accuracy for this figure, but the formation of large amounts of *iso*butylene under these conditions is unquestionable (cf. below).

(b) 10% *Aqueous acetone.* In this case a large-scale experiment was performed so that the olefin formed could be isolated, identified, and estimated in the form of its reaction products with bromine. In one experiment the dilute solution of bromine in chloroform or carbon tetrachloride, normally employed by us for olefin absorption, was replaced by a very concentrated solution (60 g. of bromine in *ca.* 200 c.c. of solution) in methylene chloride and the reaction was allowed to proceed to completion (the solvent decomposition is negligible in this case). At the conclusion of the experiment, the contents of the bromine traps were decolorised with sulphur dioxide, dried over anhydrous potassium carbonate, and distilled under reduced pressure. The main fraction (11·4 g.), b.p. 58°/32 mm., was identified as *iso*butylene dibromide (Found: C, 22·2; H, 3·8; Br, 74·4. Calc. for $C_4H_8Br_2$: C, 22·2; H, 3·7; Br, 74·1%), a smaller, less volatile fraction (4·0 g.) consisting of a bromine substitution product (Found: C, 16·3; H, 2·2; Br, 81·2. $C_4H_7Br_3$ requires C, 16·3; H, 2·4; Br, 81·3%). It was again shown in a blank experiment that under the conditions employed no appreciable amount of unsaturated material could arise from the solvent containing *tert.*-butyl alcohol and hydrogen bromide. In another experiment the *iso*butylene was collected in carbon tetrachloride at −20°, and the bromine was subsequently added drop by drop until the solution was just permanently coloured. The product, isolated as before, was substantially *iso*butylene dibromide with but a small quantity of higher-boiling material. The yield of olefin, based on isolated material, was 38%. Again, we do not claim great accuracy, but it is undeniably established that olefin elimination accompanies the hydrolysis of *tert.*-butyl bromide in aqueous acetone.

THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C. 1.

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