

249. Mechanism of Substitution at a Saturated Carbon Atom. Part VIII. Hydrolysis of *tert.*-Butyl Halides.

By KENNETH A. COOPER and EDWARD D. HUGHES.

Previous study of the unimolecular hydrolysis of *tert.*-butyl chloride is here extended to include *tert.*-butyl fluoride, bromide, and iodide. The peculiar spacing of rates observed for the halides of the *isopropyl* series (preceding paper) is reproduced in the *tert.*-butyl compounds; and, consistently with considerations of electronic structure, the rates for the tertiary halides are greater than for the corresponding secondary halides by factors of the order of 10^4 . The greater part of this difference is represented by a variation in the *B*-factor of the Arrhenius equation, $k = Be^{-E/RT}$. In 80% aqueous ethyl alcohol the *B*-factors for the *tert.*-butyl halides have the "normal" values of *ca.* 10^{13} , but the hydrolyses of the *isopropyl* halides in the same medium may be classified as "slow" unimolecular reactions, the *B* factors being of order 10^9 only. The hydrolyses of the *tert.*-butyl halides can be made "normal" or "slow" according to the solvent in which they are carried out. The results are discussed in relation to recent theories of reaction kinetics in solution.

In a previous paper (Hughes, J., 1935, 255) it was shown that the hydrolysis of *tert.*-butyl chloride in aqueous alcohol or aqueous acetone was of the first order with respect to the chloride and of zero order with respect to hydroxide ions. The explanation given was that the rate-controlling process is the ionisation of the alkyl halide, and that this is succeeded by the rapid decomposition of a solvent molecule by the *tert.*-butyl cation; the correctness of this interpretation is borne out by the investigation described in Part IX (following paper). The hydrolysis is an example of the form of substitution which we designate S_N1 .

In this paper we generalise the kinetic investigation to include the other *tert.*-butyl halides, although, on account of certain experimental difficulties, the fluoride has been studied less fully and accurately than the bromide and iodide. All four halides hydrolyse in a unimolecular fashion, with a rate independent of alkalinity or acidity, although the velocities vary over a very wide range. The rates increase from the fluoride to the iodide, but, although for the fluoride and chloride they differ by a factor of roughly 10^5 , yet for the chloride and bromide the factor is about 40, and for the bromide and iodide about 2.5. A similar variation of rate as between chloride, bromide, and iodide was also found for the S_N1 part of the hydrolysis of the *isopropyl* halides (Part VII, preceding paper). The rates for the *tert.*-butyl halides are greater than those for the corresponding *isopropyl* halides by factors all of the order 10^4 , consistently with considerations of electronic structure set forth in earlier papers of this series. In the following table we give for comparison the unimolecular rate constants for the reactions at 25° in "80%" aqueous ethyl alcohol, *i.e.*, the solvent prepared by mixing 80 vols. of anhydrous ethyl alcohol with 20 vols. of

water. The figures for *tert.*-butyl chloride come from Hughes's investigation (*loc. cit.*), and those for the *isopropyl* halides from Part VII, a calculation or estimate being applied where necessary to take account of the difference between the experimental conditions and those of the comparison. The units of k and B are sec.^{-1} , and E is in kilo-cals.

Rate Constants and Arrhenius Parameters of Unimolecular Hydrolysis of isoPropyl and tert.-Butyl Halides in 80% Aqueous Ethyl Alcohol.

	<i>isoPropyl</i> halides.			<i>tert.</i> -Butyl halides.		
	k_{25}^*	B	E	k_{25}^*	B	E
Fluoride	—	—	—	$ca. 10^{-10} \ddagger$	—	—
Chloride	1.9×10^{-9}	2.1×10^8	23.2	9.14×10^{-6}	7.8×10^{11}	23.1
Bromide	5.8×10^{-8}	6.5×10^9	23.2	3.74×10^{-4}	2.0×10^{13}	22.8
Iodide	6.2×10^{-8}	$4.5 \times 10^{10} \dagger$	24.3 \ddagger	9.01×10^{-4}	2.6×10^{13}	22.4

* Calculated from experiments at higher temperatures.

† Estimated from experiments in "60%" alcohol.

‡ Roughly estimated from experiments at a higher temperature.

The rate constants for the *tert.*-butyl halides are composite inasmuch as a small proportion of the reaction measured is due to olefin elimination* (cf. this vol., p. 1280), and ethoxylation accompanies hydroxylation. However, we are of the opinion that the rate-controlling process in all these reactions is the ionisation of the alkyl halide, and, as we are here concerned with the rate of ionisation rather than with the fate of the ions, the figures recorded in the table form the proper basis for comparison.

In the case of *tert.*-butyl bromide and iodide we have measured the temperature coefficient of reaction velocity, and applied the equation, $k = Be^{-E/RT}$. The values of B and E thus obtained, together with the available values of these quantities for the *isopropyl* halides and *tert.*-butyl chloride, are included in the table.

The most noteworthy feature of these figures is the close grouping of all the E -values around 23 kilo-cals. The greater part of the difference in the rate constants can be represented by means of variations in the B factors. One would expect that structural changes of the type investigated would cause a variation in both parameters, and we believe that the zero-point critical energy does vary as between the *isopropyl* and *tert.*-butyl halides, and as between chlorides, bromides, and iodides, but for reasons indicated elsewhere (Hughes, Ingold, and Shapiro, J., 1936, 225) we are not able to deduce this from the Arrhenius critical energies. In this connection it may be noted that Evans and Polanyi (*Trans. Faraday Soc.*, 1936, **32**, 1333) have concluded that, in the case of related reactions in solution, a sequence of zero-point critical energies, calculated from considerations of atomic mechanism, cannot always be expected to bear a simple relationship to the observed critical energies, if, as is usual, the latter are measured at ordinary temperatures. Indeed, they infer that the quantity which can be most easily related to the zero-point critical energy is $\log k$ (k = the reaction velocity constant)—a conclusion which is in entire agreement with our experience. The normal value of the B factor of a unimolecular reaction is about $10^{13} \text{ sec.}^{-1}$ (Polanyi and Wigner, *Z. physikal. Chem.*, 1928, **139**, 439), and this is practically the value we find for the reactions of the *tert.*-butyl halides. For the *isopropyl* halides the B values are smaller by 10^3 — 10^4 , so that these reactions may be said to qualify for inclusion in the category of "slow" unimolecular reactions. In the language of the transition state theory, a greater restriction is placed on the co-ordinates of the transition state in the reactions of the *isopropyl* than in those of the *tert.*-butyl halides. One can see in a general way that a more facile electron supply to the halogen atom would be expected to increase the variation permissible in the co-ordinates of those molecules, particularly the solvent molecules, which are concerned in an ionisation. Viewing the matter from a somewhat different standpoint, we may say that the *isopropyl* halides require a more specific orientation of solvent molecules to produce a field capable of stabilising the polar transition complex (cf. Hinshelwood and Winkler, J., 1936, 371). The variation of the B factors between different halides belonging to the same alkyl group is smaller,

* The olefin elimination was not detected in the earlier investigation on *tert.*-butyl chloride (*loc. cit.*).

viz., $10-10^2$ over the range chlorides to iodides, and the trend is towards larger values for the heavier halogens. The large difference of rate between chloride and fluoride could not be analysed in terms of the Arrhenius parameters on account of the inactivity and volatility of *tert.*-butyl fluoride, but the phenomenon would appear to merit investigation in a system more easily amenable to experimental treatment.

We expect solvent co-ordinates to be especially important in the definition of the transition states of reactions dependent on ionisation, and we can illustrate the truth of this assumption by reference to an effect which, in its magnitude, is unparalleled in any bimolecular hydrolysis with which we are acquainted. When the solvent used in the hydrolysis of *tert.*-butyl bromide is changed from 80% ethyl alcohol to 95% acetone, the Arrhenius critical energy undergoes only an insignificant change, whilst the *B* factor falls from 2.0×10^{13} to 9.2×10^{10} . A similar effect was observed in the influence of the solvent on the hydrolysis of *tert.*-butyl chloride (Hughes, *loc. cit.*). It is clear that the reaction is one which can be made "normal" or "slow," according to the solvent in which it is carried out. This shows that the replacement of a more ionising by a less ionising medium places narrower limits on the co-ordinates defining the transition state, a conclusion which would be unintelligible unless these co-ordinates included in an essential way those of solvent molecules.

These observations support the view, now becoming prevalent amongst investigators in the field of reaction kinetics, that the so-called "slow" reactions are but extremes in a continuous range of reactions in which the *B*-factors may vary within wide limits. Even in reactions of one type, such as the one herein discussed, we could traverse this range by making suitable changes in the structure of the reactants and in the properties of the medium.

EXPERIMENTAL.

tert.-Butyl Fluoride.—A mixture of *tert.*-butyl alcohol (50 g.) and aqueous hydrofluoric acid (50–60%, 50 g.) was warmed to 60° in a copper flask. The volatile product was condensed in a freezing mixture of ice and salt, treated with bromine at 0° to remove an unsaturated impurity (probably *isobutylene*), and distilled, head and tail fractions being neglected. The fluoride is a gas at room temperature; the liquid has b. p. *ca.* 13°/760 mm. On prolonged standing at 0° it eliminates hydrogen fluoride and forms unsaturated products—a reaction which is greatly accelerated by phosphoric oxide or sulphuric acid.

tert.-Butyl chloride was prepared as described in Part V (*loc. cit.*).

tert.-Butyl bromide was prepared by a modification of Norris's method (*Amer. Chem. J.*, 1907, **38**, 641). The crude bromide, which separates when *tert.*-butyl alcohol is mixed with concentrated aqueous hydrobromic acid (*d* 1.7), was removed, saturated with gaseous hydrogen bromide, dried over anhydrous sodium carbonate, and distilled from the same reagent, b. p. 72°/760 mm.

tert.-Butyl Iodide.—Dry hydrogen iodide, prepared by adding concentrated aqueous hydriodic acid (*d* 1.9) to phosphoric oxide mixed with red phosphorus, was passed into *tert.*-butyl alcohol at room temperature. When the separation into two layers appeared to be complete, the organic layer was again saturated with hydrogen iodide, dried over anhydrous sodium carbonate, and fractionated under reduced pressure.

Media.—Commercial absolute ethyl alcohol was dried by the method of Lund and Bjerrum (*Ber.*, 1931, **64**, 210), and fractionated. The "50%" aqueous ethyl alcohol was made by mixing equal volumes of this alcohol and water, and the "80%" aqueous alcohol by mixing 8 l. of alcohol with 2 l. of water. The "95%" acetone was made by mixing 950 c.c. of acetone, purified by the method of Conant and Kirner (*J. Amer. Chem. Soc.*, 1924, **46**, 246), with 50 c.c. of water. The unimolecular hydrolyses investigated are extremely sensitive to changes in the composition of the medium; but in all cases in which a strict comparison of rates was desirable, portions of the same sample of the aqueous medium were used.

Isolation of Ethyl tert.-Butyl Ether.—*tert.*-Butyl bromide (25 c.c.) was diluted to 250 c.c. at 25° with "80%" aqueous ethyl alcohol. When the reaction was complete the mixture was neutralised with sodium carbonate and distilled. The first fraction, b. p. below 82°, was diluted with water, and the small upper layer containing ethyl *tert.*-butyl ether was removed, boiled under reflux with sodium, and distilled, b. p. 69°/760 mm. (Found: C, 70.0; H, 13.5. Calc.: C, 70.6; H, 13.7%). The yield, calculated from the weight of *tert.*-butyl bromide used, was 13 mols. %, but this is a minimum figure for the amount of ether formed.

Estimation of Olefin.—By employing the method of analysis described in Part VI (Hughes, Ingold, and Shapiro, J., 1936, 225), olefin was detected in the hydrolysis of *tert.*-butyl chloride, bromide, and iodide (*tert.*-butyl fluoride was not examined). In "80%" aqueous ethyl alcohol at 25° the yield was *ca.* 15% of the total hydrolysis.

Kinetic Measurements.—The thermostats could be set to within 0.05°. Two methods of procedure were employed. In the first, a suitable quantity of the halide was dissolved in the initially neutral or alkaline medium at the desired temperature, and, at suitable intervals, 5 c.c. portions were withdrawn, run into 100 c.c. of cold absolute alcohol or acetone to stop the reaction, and analysed by titration against standard acid or alkali as required. In the second, portions of 5 c.c. of the reaction mixture were enclosed in sealed tubes, which were placed in the thermostat for known times and then broken under absolute alcohol, and estimated. The latter method was used where there was a danger of loss by evaporation. The reactions proceeded to completion with the exception of the hydrolysis of *tert.*-butyl bromide in 95% acetone. In this case a stationary state was reached after 95% of the halide had been hydrolysed, but the initial rate constants were not affected.

Hydrolysis of tert.-Butyl Bromide.—The results are summarised in Table I. Measurements were made in "80%" aqueous ethyl alcohol (Sample A) at three temperatures (Expts. 1, 2, and 3) and in "95%" acetone at two temperatures (Expts. 6 and 7). In the former medium the method of pipetting the samples was used, and in the latter the sealed-tube method. The first-order rate constants are calculated from the formula $k_1 = (1/t) \cdot \log_e \{a/(a-x)\}$, where a is the initial concentration of *tert.*-butyl bromide and x the decrease in its concentration. In "80%" alcohol, a was found by determining the asymptotic value of x after long times, and in "95%" acetone it was obtained by running 5 c.c. portions of the reaction mixture into about 50 c.c. of water to complete the hydrolysis and estimating acidity in the usual way. Expts. 4 and 5 show that the first-order constant in "80%" aqueous ethyl alcohol (sample B) is the same in acid and alkaline solution. In "95%" acetone the Arrhenius equation takes the form $k = 9.16 \times 10^{10} e^{-22,700/RT}$, where k and B are in sec.^{-1} and E is in cal. The Arrhenius parameters for the hydrolysis in "80%" alcohol are given in the introduction. The results of two typical experiments are recorded in detail in Table II.

Hydrolysis of tert.-Butyl Iodide.—Measurements were made in "80%" aqueous ethyl alcohol (Sample A) at two temperatures (Table I, Expts. 8 and 9) and in acid and alkaline solutions (Sample C, Expts. 10 and 11). The method of pipetting samples was used, and a was taken as the asymptotic value of x after long times. The Arrhenius parameters are given in the theoretical section.

Hydrolysis of tert.-Butyl Fluoride.—Measurements were made in "50%" aqueous ethyl alcohol at 100° by the sealed-tube method. The reaction is heterogeneous under these conditions (liquid and gaseous phases are present), and the velocity is dependent on the volume of the tubes. Notwithstanding that tubes of approximately equal volumes were used in the experiments recorded, the first-order rate "constants" are erratic. The average constants obtained in two experiments in alkaline solution are shown in Table I (Expts. 12 and 13), and a typical experiment is recorded in detail in Table II. The difference between the two rate constants may be due to the effect of the base on the solubility of the fluoride in the liquid phase. For obvious reasons, only the initial stages of the hydrolysis in initially neutral solution could be examined, but the rate was substantially the same as that in dilute alkaline solution.

TABLE I.

Summary of first-order rate constants. k_1 is in sec.^{-1} .					
Expt.	Halide.	Medium.	Initial [NaOH].	Temp.	$k_1 \times 10^6$.
1	Bu γ Br	80% EtOH (A)	—	24.95°	374
2	"	"	—	15.05	100
3	"	"	—	0.10	11.2
4	"	80% EtOH (B)	—	24.95	364
5	"	"	0.14N	"	357
6	"	95% C ₂ Me ₂	—	"	2.10
7	"	"	—	50.0	41.0
8	Bu γ I	80% EtOH (A)	—	24.95	901
9	"	"	—	0.10	28.8
10	"	80% EtOH (C)	—	25.15	913
11	"	"	0.15N	"	920
12	Bu γ F	50% EtOH	0.17N	100°	3.0
13	"	"	0.06N	"	7.9

TABLE II.

Illustrating determination of first-order rate constants. $[\text{Bu}\gamma\text{X}]$ expressed as equivalent c.c. of $N/20\text{-NaOH}$ (1, 2, and 3) or $N/50\text{-HCl}$ (4) per 5 c.c. of solution. k_1 is in sec.^{-1} .

1. Hydrolysis of $\text{Bu}\gamma\text{Br}$ in "80%" alcohol (A) at 24.95° . $[\text{NaOH}]_{t=0} = 0$.											
t (secs.)	0	326	660	926	1470	1800	2390	3010	3596	5355	∞
$[\text{Bu}\gamma\text{Br}]$	8.28	7.34	6.51	5.81	4.83	4.31	3.43	2.70	2.09	1.13	0
$k_1 \times 10^4$	—	3.70	3.64	3.82	3.67	3.62	3.69	3.72	3.83	3.72	—
2. Hydrolysis of $\text{Bu}\gamma\text{Br}$ in "95%" acetone at 50.0° . $[\text{NaOH}]_{t=0} = 0$.											
t (mins.)	0	79	146	203	289	375	474	∞			
$[\text{Bu}\gamma\text{Br}]$	11.97	9.85	8.39	7.27	5.89	4.78	4.13	0.64			
$k_1 \times 10^5$	—	4.08	4.06	4.10	4.09	4.08	(3.75)	—			
3. Hydrolysis of $\text{Bu}\gamma\text{I}$ in "80%" alcohol (A) at 0.10° . $[\text{NaOH}]_{t=0} = 0$.											
t (mins.)	0	29.7	62.4	124	180	240	300	389	∞		
$[\text{Bu}\gamma\text{I}]$	7.60	7.22	6.83	6.17	5.62	5.00	4.51	3.77	0		
$k_1 \times 10^5$	—	2.95	2.82	2.80	2.80	2.91	2.90	3.00	—		
4. Hydrolysis of $\text{Bu}\gamma\text{F}$ in "50%" alcohol at 100° . $[\text{NaOH}]_{t=0} = 0.17N$.											
t (hrs.)	0	2.90	5.90	8.92	16.42	26.42	51.23	73.37	∞		
$[\text{Bu}\gamma\text{F}]$	15.90	15.42	15.27	14.53	13.48	12.06	8.90	6.40	0		
$k_1 \times 10^8$	—	2.94	(1.91)	2.81	2.81	2.92	3.14	3.44	—		

UNIVERSITY COLLEGE, LONDON.

[Received, April 24th, 1937.]