261. *The Mechanism of Elimination Reactions. Part IV. Unimolecular Olefin Formation from* tert.*-Amyl Halides in Acid and Alkaline Aqueous Solutions, and Some Remarks on the Scope of the Unimolecular Mechanism.*

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tert.-Amyl chloride, bromide and iodide exhibit unimolecular substitution (this vol., p. 1177) and unimolecular elimination (this vol., p. 1271) in hydrolysis, and present cases particularly favourable to quantitative investigation of the unimolecular elimination. The kinetic properties of the simultaneous reactions of the halides are investigated.

The rate constants of the *tert.*-amyl halides are all higher than those of the corresponding *tert.*-butyl halides (preceding paper), and increasing alkylation leads to an increasing preference for the elimination reaction. For a given halogen atom, the change of alkyl groups alters the ratio of the rates of substitution and elimination by a factor of the same order as that which measures the alteration in the individual rates; whereas the change of the halogen atom may alter the order of magnitude of the rates, but, for a given alkyl group, leaves the rate-ratio almost unchanged. The results support the hypothesis that the division of the reaction between substitution and elimination occurs essentially after the separation of the alkyl group from the halogen atom (cf. preceding papers).

In acid solution equilibria are set up subsequently to the original hydrolysis: the olefin becomes hydrated and the alcohol dehydrated by reactions which are considered to be specialised forms of the substitution and elimination processes herein discussed. Some further cases of unimolecular elimination are cited.

A SURVEY of the literature having shown that the hydrolysis of *tert.*-amyl halides, even under conditions expected to lead to first-order kinetics, involves much olefin elimination, it appeared that a kinetic study of these reactions would be of assistance in the elucidation of the mechanism of elimination, and provide a specially favourable case in which to test the theory of a common slow stage in unimolecular elimination and substitution (see Parts II and III). Furthermore, since the rates of the unimolecular hydrolysis and elimination reactions of the *tert.*-butyl halides are known (Hughes, J., 1935, 255; Cooper and Hughes, this vol., p. 1183; Cooper, Hughes, and Ingold, this vol., p. 1280), the study of the *tert.*-amyl halides must show the effect of increased alkylation on the rates of these reactions. Yet another motive for the present work was our desire to prepare the ground for an investigation into the preferential elimination of isomeric olefins from a branched-chain hydrocarbon radical, and for this also the *tert.*-amyl halides commended themselves.

It is well known that the *tert.*-amyl halides hydrolyse easily, and that *tert.*-amyl alcohol and unsaturated hydrocarbons may, under certain conditions, be isolated from the products. Thus the hydrolysis of the iodide with cold water is said to give *tert.*-amyl alcohol (Bauer, *Annalen*, 1883, **220**, 158), while a mixture of trimethylethylene and *as.*-methylethylethylene is reported to be obtainable with the agency of hot alcoholic potassium hydroxide (Wagner, *Ber.*, 1888, **21**, 1230; Kondakoff, *J. pr. Chem.*, 1896, **54**, 442; *J. Russ. Phys. Chem. Soc.*, 1889, **21**, 78; and others). Recently, Woodburn and Whitmore (*J. Amer. Chem. Soc.*, 1934, **56**, 1394) treated *tert.*-amyl chloride and bromide with water and with acidic and basic reagents, and obtained varying proportions of *tert.*-amyl alcohol and trimethylethylene, depending on the conditions used. In the case of the chloride it was shown that the hydrolysis proceeded with almost the same velocity whether the reagent was dilute sodium carbonate, water, or dilute sulphuric acid. Two liquid phases were present in these experiments; nevertheless the results mentioned indicate that the total decomposition is of the first order, its speed being independent of reagent anions; and this must be true for the formation of both alcohol and olefin, since each is produced in large amount. French and Schaefer (*J. Amer. Chem. Soc.*, 1935, **57**, 1576) determined the proportions of olefin formed when *tert.*-amyl chloride and bromide were stirred heterogeneously at 35° and 45° with aqueous solutions of barium hydroxide (0·20—0·25*M*), and concluded that an increase in the concentration of the base results in an increase in the percentage of olefin. It is significant, however, that if we omit from consideration their experiments with silver oxide, where a different mechanism is operative (cf. this vol., pp. 1237, 1243, 1252), approximately the same amount of olefin was obtained with all the reagents they used; it was the same, for instance, with a sparingly soluble base like calcium hydroxide as with sodium hydroxide.

All our measurements were made in homogeneous solution; and, with the exception of olefin formation in the hydrolysis of *tert.*-amyl iodide, they include a kinetic investigation of both the total reaction and the olefin elimination for the chloride, bromide, and iodide, in acid and in alkaline solution. Most of the measurements were carried out in 80% alcohol at 25°, but, in the case of the chloride, experiments were also made at 50° and in 60% alcohol. The results are summarised in Table I. The headings of the first three cols. are self-explanatory. Cols. 4 and 5 give the initial concentrations of the reagents specified. Col. 6 records the average first-order velocity coefficient (k_1) for the total reaction in sec.$^{-1}$, and cols. 7 and 8 give the analogous coefficients for the constituent processes of elimination (k_{E1}) and substitution (k_{S_N1}) in the same units; k_1 and k_{E1} were determined separately, and k_{S_N1} was obtained by difference. The last col. gives the ratio of the elimination reaction to the total decomposition.

TABLE I.

Summary of the First-order Rate Constants of the Hydrolysis of the tert.*-Amyl Halides.*

Expt.	Halide.	Medium.	Temp.	[Halide].	[NaOH].	10^5k_1.	10^5k_{E1}.	$10^5k_{S_N1}$.	k_{E1}/k_1.
1	Am$^{\gamma}$Cl	80% aq.-alc.	25·2°	0·161	—	1·40	0·459	0·941	0·328
2	,,	,,	,,	0·0787	—	1·50	0·500	1·00	0·333
3	,,		,,	0·0776	0·212	1·52	0·515	1·01	0·339
4	,,		50·0	0·1471	—	28·5	11·5	17·0	0·403
5	,,	60% aq.-alc.	25·2	0·0783	—	14·8	3·81	11·0	0·257
6	Am$^{\gamma}$Br	80% aq.-alc.	,,	0·0722	—	58·3	15·3	43·0	0·262
7	,,	,,	,,	0·0654	0·118	58·0	17·9	40·1	0·308
8	Am$^{\gamma}$I	,,	,,	*ca.* 0·13	—	174	45·2	128·8	0·260
9	,,	,,	,,	*ca.* 0·12	0·12	178	43·8	134·2	0·246

The unimolecular nature of both the total reaction and the elimination was proved for the chloride by the constancy of the first-order rate coefficients, and by the ineffectiveness of alkali. The slight differences in the velocity constants recorded in experiments 1 and 2 are undoubtedly to be attributed to a medium effect (cf. Hughes, *loc. cit.*). Similar, but less extended, tests established the unimolecular nature of the reactions of the bromide and the iodide. The slight effect of alkali on the velocity of the elimination reaction of the bromide appears to be connected with the ratio in which the total decomposition is divided between substitution and elimination, and not with the incursion of a second-order elimination process. This is indicated by the fact that the rate of the total reaction is not altered by the alkali.

Our results indicate how physical conditions control the proportions in which the alkyl halide undergoes elimination and substitution *: measurements on *tert.*-amyl chloride were carried out at two temperatures and in two aqueous-alcoholic media of different water content, and the results showed that olefin elimination is favoured relatively to the substitution by an increase in temperature and by a low water content in the medium.

We compare in Table II the rate constants for the *tert.*-amyl halides with those obtained for the *tert.*-butyl halides under similar conditions (previous paper). The medium in each case was 80% alcohol and the temperature was 25·0° for the *tert.*-butyl halides and 25·2° for the *tert.*-amyl halides. The first-order constants are in sec.$^{-1}$.

TABLE II.

First-order Rate Constants of the Hydrolysis of the tert.*-Butyl and* tert.*-Amyl Halides.*

	tert.-Butyl halides.				*tert.*-Amyl halides.			
	10^5k_1.	10^5k_{E1}.	$10^5k_{S_N1}$.	k_{E1}/k_1.	10^5k_1.	10^5k_{E1}.	$10^5k_{S_N1}$.	k_{E1}/k_1.
Chloride	0·854	0·144	0·710	0·168	1·50	0·50	1·00	0·333
Bromide	37·2	4·69	32·5	0·126	58·3	15·3	43·0	0·262
Iodide	90·1	11·6	78·5	0·129	174	45·2	128·8	0·260

Several interesting relationships emerge from this comparison. First, in each alkyl series there are much larger velocity differences between chloride and bromide than between bromide and iodide, and this is true of all the velocity coefficients recorded. This phenomenon appears to be general and has already been discussed for the reactions of the *iso*propyl halides, and the total reaction of the *tert.*-butyl halides (Hughes and Shapiro, this vol., p. 1177; Cooper and Hughes, this vol., p. 1183). Secondly, the rate constants for the *tert.*-amyl halides are all larger than the corresponding constants for the *tert.*-butyl halides. The reaction is obviously one which is facilitated by electron release to the halogen atom, and in this example the inductive effect of the additional methyl group present in the *tert.*-amyl halides outweighs any effect of opposite kind such as that postulated by Baker and Nathan (J., 1935, 1844). The apparently much smaller reactivity

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* The substitution is composite in that both *tert.*-amyl alcohol and ethyl *tert.*-amyl ether are formed in aqueous ethyl alcohol.

of *tert.*-amyl than of *tert.*-butyl chloride, observed by Woodburn and Whitmore (*loc. cit.*) in their experiments in heterogeneous solution, must, as these authors suggest, be due to the smaller solubility of the higher homologue in the aqueous phase; the apparent stability of *tert.*-amyl chloride in heterogeneous hydrolysis was also observed by French and Schaefer (*loc. cit.*). Thirdly, the ratios k_{E1}/k_1 are approximately twice as great for the *tert.*-amyl halides as for the *tert.*-butyl compounds, so that increasing alkylation evidently leads to an increasing preference for the elimination reaction. This fact is of importance in relation to the question of the preferential elimination of isomeric olefins from branched-chain hydrocarbon radicals, a question which is being investigated.

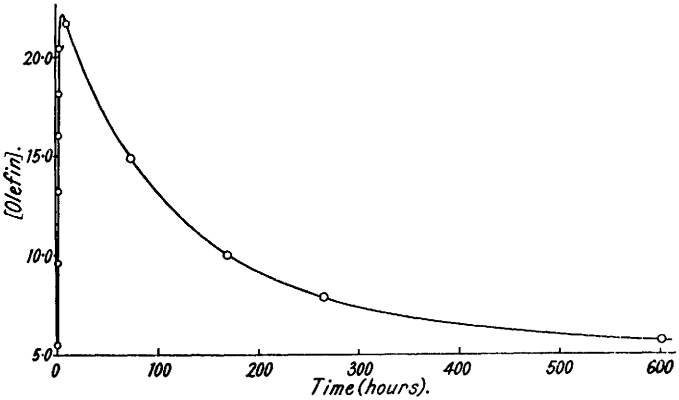
The relative constancy in the k_{E1}/k_1 ratios exhibited by different halides containing a common alkyl radical, already pointed out for the *sec.*-octyl and *tert.*-butyl halides, is again shown by the *tert.*-amyl halides. Table II brings into contrast the effects obtained by changing the alkyl group and the halogen atom. When we change the alkyl group from *tert.*-butyl to *tert.*-amyl the individual rates change by factors of 1½—4, and the k_{E1}/k_1 ratio by a factor of 2 : the change in the ratio is of the same order as the change in the rates. When however, in either alkyl series, we replace chlorine by bromine or iodine the rates change by factors of 30—130, and yet the k_{E1}/k_1 ratio remains constant to within a factor of 1·3. This contrast forms strong support for the hypothesis that the division of the reaction between substitution and elimination occurs essentially after the separation of the alkyl group from the halogen atom (cf. Parts II and III).

A complication arose in the experiments in acidic solutions owing to the disappearance of a portion of the olefin. No such disturbance was encountered in any of the experiments in alkaline solution, and there is little doubt that it is due to acid-catalysed hydration of the hydrocarbon. This reaction is well established : it was studied by Butlerow in his experiments on *iso*butylene and trimethylethylene (*Annalen*, 1867, **144**, 34; 1877, **189**, 44), and a kinetic investigation has recently been carried out by Lucas and his collaborators (Lucas and Eberz, *J. Amer. Chem. Soc.*, 1934, **56**, 460, 1230; Lucas and Liu, *ibid.*, p. 2138). These authors concluded that the reaction was of the first order with respect to both the olefin and the acid, and in the case of *iso*butylene was measurably reversible. One would expect that the disappearance of the olefin in acidic media is likely to disturb the observation of its formation from the halide most seriously when the concentration of the latter is low and that of the hydrocarbon and of the acid is high, *i.e.*, towards the end of hydrolysis; and this has been our experience. The greatest interference was experienced in the hydrolysis of the chloride in 80% aqueous ethyl alcohol at 25·2°; but even in this case only the second half of the reaction was noticeably affected, and the difficulty could be overcome (cf. p. 1289). In the hydrolysis of the chloride in 80% alcohol at 50°, and in 60% alcohol at 25°, the disturbance became appreciable only towards the end of the reaction. The hydrolysis of the bromide and the iodide, being much faster than that of the chloride, was not affected, although the hydration was observed after the initial reaction had completed its course. Our results also establish the reversibility of the hydration, although, on account of its extreme slowness in the ultimate stages, we cannot say with certainty that equilibrium was reached in any of our experiments. This is illustrated in the annexed plot of olefin concentration against time. The steep ascending portion of the curve represents the formation of olefin from the halide, and the descending portion, which becomes asymptotically parallel to, but displaced from, the time-axis, represents the reversible hydration of the hydrocarbon.

The reactions here exemplified may be interpreted as follows. The initial process is the ionisation of the halide, and the hydrocarbon cation either unites with an anion or loses a proton. These are the unimolecular substitution and elimination reactions of the halide (S_N1 and E1). The total reaction is of the first order (R = Alk. or H) :

$$\left.\begin{array}{l} \mathrm{CR_2H{\cdot}CR_2{\cdot}Hal.} \xrightarrow{\text{slow}} \mathrm{CR_2H{\cdot}CR_2^+ + Hal.^-} \\ \mathrm{CR_2H{\cdot}CR_2^+} \left\{ \begin{array}{l} \xrightarrow{\text{fast}} \mathrm{CR_2H{\cdot}CR_2{\cdot}OH} \quad (\mathrm{S_N1}) \\ \xrightarrow{\text{fast}} \mathrm{CR_2{:}CR_2 + H^+} \quad (\mathrm{E1}) \end{array}\right. \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In alkaline solution this is all that happens. In acid solution, however, each of the two products undergoes further change dependent on proton transfer. First, the alcohol forms an oxonium ion, and then undergoes slow ionisation, analogously to the chloride, with resulting unimolecular substitution and elimination (S_N1 and E1). The total reaction is of the second order, being of the first with respect to hydrogen ions and the first with respect to alcohol:



Illustrating the formation of olefin in the hydrolysis of tert.*-amyl chloride, and its subsequent hydration. Solvent:* 80% *aqueous ethyl alcohol. Temp.* 50·0°. *Initially* [AmγCl] = 0·1471*N and solution neutral.* [*Olefin*] *expressed in equivalent c.c. of* 0·04904*N*-$Na_2S_2O_3$ *per* 10 *c.c. of solution.*

$$\left.\begin{aligned} CR_2H{\cdot}CR_2{\cdot}OH + H^+ &\overset{\text{fast}}{\rightleftharpoons} CR_2H{\cdot}CR_2{\cdot}OH_2^+ \\ CR_2H{\cdot}CR_2{\cdot}OH_2^+ &\xrightarrow{\text{slow}} CR_2H{\cdot}CR_2^+ \\ CR_2H{\cdot}CR_2^+ &\begin{cases} \xrightarrow{\text{fast}} CR_2H{\cdot}CR_2{\cdot}OH & (S_N1) \\ \xrightarrow{\text{fast}} CR_2{:}CR_2 + H^+ & (E1) \end{cases} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Unimolecular substitutions in 'onium salts are well established (Hughes and Ingold, J., 1933, 69, 1571; 1935, 244; Hughes, Ingold and Patel, J., 1933, 526; Gleave, Hughes and Ingold, J., 1935, 236). The one here represented is not ordinarily observable, but it amounts to an acid-catalysed exchange of hydroxyl between the alcohol and water, and is being studied in these laboratories with the aid of heavy-oxygen water. Unimolecular elimination has not yet been kinetically established for 'onium salts generally,* but the extension of the work on the halides will include its study.

Secondly, the olefin forms a hydrocarbon cation, which then decomposes in the same two ways. This reaction is of the second order, being of the first order with respect to hydrogen ions and the first order with respect to olefin:

$$\left.\begin{aligned} CR_2{:}CR_2 + H^+ &\xrightarrow{\text{slow}} CR_2H{\cdot}CR_2^+ \\ CR_2H{\cdot}CR_2^+ &\begin{cases} \xrightarrow{\text{fast}} CR_2H{\cdot}CR_2{\cdot}OH & (S_N1) \\ \xrightarrow{\text{fast}} CR_2{:}CR_2 & (E1) \end{cases} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The first reaction is a hydration, and the second, not ordinarily observable, could be investigated (if one of the groups written as R were hydrogen) with the aid of deuterium as an acid-catalysed hydrogen-exchange. In acid solution, then, the reaction systems (2) and (3) operate in addition to (1); indeed, (1) and (2) supply the olefin required for (3), whilst (1) and (3) provide the alcohol necessary for (2). A consideration of these schemes, and a knowledge of the ratio in which the cation partitions itself between substitution and elimination, should form an adequate guide in predicting the course of hydrolysis under given circumstances. The general result will always be that in the first phase of reaction halide

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* We include in this category the acid-catalysed decomposition of certain ethers.

disappears and alcohol and olefin are formed. The proportion in which they are formed will, however, be determined by the cation partition ratio, and will not be the equilibrium proportion. In acid solution a second phase of reaction supervenes and in this the alcohol and olefin come into equilibrium. In the figure the rising branch of the curve shows the formation of olefin in the first phase (reactions 1), whilst the falling branch illustrates the equilibration of olefin with alcohol during the second phase (reactions 2 and 3).

As an example we may consider a statement by Woodburn and Whitmore (*loc. cit.*) : "The hydrolysis of tertiary chlorides with hot water or sodium carbonate solution gives olefin exclusively. With *cold* water or *cold* sodium hydroxide solution, a certain amount of tertiary alcohol is formed with the olefin." In alkaline solution the only reactions are the irreversible processes (1), and, in view of the olefin/alcohol ratios exhibited by the *tert.*-butyl and the *tert.*-amyl chlorides, the remark concerning sodium carbonate cannot be generally true. In the absence of alkali, the production of acid brings in reactions 2 and 3, which would set up an equilibrium between the alcohol and the olefin, and the validity of the statement relating to the effect of hot water would appear to depend on the possible circumstance that the olefin, being volatile in the *hot* water, may be removed as it is formed, and thus produced quantitatively.

A probable example of unimolecular elimination and substitution, which involves neither a halide nor an 'onium compound but the ester of a strong acid, is the etherification of ethyl alcohol in the presence of sulphuric acid. We suppose that the ethyl hydrogen sulphate ionises; and that the cation, in the presence of alcohol, gives ether; otherwise it gives ethylene :

$$C_2H_5{\cdot}O{\cdot}SO_3H \xrightarrow{\text{slow}} C_2H_5^+ + O{\cdot}SO_3H^-$$

$$C_2H_5^+\begin{cases} \xrightarrow{\text{fast}} C_2H_5{\cdot}OC_2H_5 \quad . \ . \ . \ . \ . \ . \ . \quad (S_N1) \\ \xrightarrow{\text{fast}} C_2H_4. \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (E1) \end{cases}$$

It may be noted in this connexion that the $\cdot SO_3R$ group has so great a tendency to ionise that unimolecular processes are expected, not only for secondary and tertiary alkyl esters, but also for ethyl, and even the methyl, compounds.

EXPERIMENTAL.

tert.-*Amyl Halides.*—The products obtained by shaking *tert.*-amyl alcohol with the concentrated halogen acids were saturated with the gaseous hydrogen halide, and distilled from anhydrous potassium carbonate.

Media.—Commercial absolute ethyl alcohol was dried by the method of Lund and Bjerrum (*Ber.*, 1931, **64**, 210), and the aqueous mixtures were made up by volume as described previously (cf. this vol., p. 1179).

Kinetic Measurements.—In the experiments at 25·2° the halide was dissolved in the initially neutral or alkaline medium. At suitable intervals portions were run each into 100 c.c. of absolute alcohol or acetone, and the acid or alkali titrated with standard sodium hydroxide or hydrochloric acid, lacmoid being used as indicator. At similar intervals equivalent portions were run each into 150 c.c. of carbon tetrachloride, and the olefin was estimated as described in the preceding paper. In the experiments at 50·0° portions of the reaction mixtures were enclosed in sealed tubes which were placed in the thermostat for known times, broken under absolute alcohol or carbon tetrachloride as required, and analysed as before.

Hydrolysis of tert.-*Amyl Chloride.*—Typical experiments are recorded in Table III. The first three cols. are self-explanatory. Col. 4 gives the mol.-ratio of olefin to total reaction, and col. 5 the total first-order rate constant ($k_{E1} + k_{S_N1}$) calculated from the formula $k_1 = (1/t).\log_e\{a/(a - x)\}$, where a is the initial concentration of *tert.*-amyl chloride and x the decrease in concentration; a was found by determining the asymptotic value of x (the [HCl]) at large times. In the experiment in alkaline solution (Table III, B), which is not affected by the hydration of the olefin, this constant (k_1') was also determined in a similar manner from the results of the olefin estimations (cf. Part II). Col. 6 records the first-order rate coefficients of the elimination reaction; these are obtained by multiplying the coefficients in col. 5 by the ratios in col. 4. The constants are in sec.$^{-1}$ except where otherwise stated. The hydration of the olefin is illustrated in subsidiary tables.

TABLE III.

Illustrating determination of first-order rate constants of the hydrolysis of tert.*-amyl chloride, and the hydration of the olefinic product.*

A. Solvent: 80% aqueous alcohol. Temp. 25·2°. Initially [Am$^\gamma$Cl] = 0·0787*N*, and solution neutral. Samples of 20 c.c. titrated. [HCl] expressed as equivalent c.c. of 0·1069*N*-NaOH and [Olefin] as c.c. of 0·0486*N*-$Na_2S_2O_3$.

t (hrs.).	[HCl].	[Olefin].	E1/(E1+S_N1).	10^7k_1.	10^7k_{E1}.	*t* (hrs.).	[HCl].	[Olefin].	E1/(E1+S_N1).	10^7k_1.	10^7k_{E1}.
3·00	2·17	3·00	0·314	148	46·5	8·00	5·17	7·73	0·340	150	51·0
4·00	2·84	4·18	0·335	149	49·9	9·00	5·72	8·40	0·334	152	50·7
5·10	3·54	5·08	0·326	150	48·9	10·00	6·16	9·19	0·339	151	51·2
6·00	4·06	5·96	0·334	149	49·8	11·00	6·56	10·00	0·347	149	51·7
7·00	4·63	6·78	0·333	150	50·0						

t (hrs.)	25·0	27·0	29·0	73·5	99·0	124	196	298	445
[HCl]	11·16	11·56	11·76	14·42	14·67	14·71	14·75	14·72	14·72
[Olefin]	13·17	13·58	15·01	16·81	16·79	16·01	15·21	13·56	13·49
E1/(E1 + S_N1)	0·268	0·267	0·290	0·265	0·260	0·247	0·234	0·209	0·208

B. Solvent: 80% aqueous alcohol. Temp. 25·2°. Initially [Am$^\gamma$Cl] = 0·0776*N*, and [NaOH] = 0·212*N*. Samples of 20 c.c. titrated. [HCl] (as NaOH neutralised) expressed in c.c. of 0·1564*N*-HCl and [Olefin] as c.c. of 0·050*N*-$Na_2S_2O_3$.

t (hrs.).	[HCl].	[Olefin].	E1/(E1+S_N1).	10^7k_1.	10^7k_{E1}.	$10^7k_1'$.	*t* (hrs.).	[HCl].	[Olefin].	E1/(E1+S_N1).	10^7k_1.	10^7k_{E1}.	$10^7k_1'$
4·00	1·89	4·40	0·372	147	54·6	163	28·1	8·00	16·85	0·337	161	54·3	160
5·00	2·36	5·15	0·349	151	52·7	156	29·3	8·02	16·78	0·334	157	52·4	152
6·00	2·88	5·93	0·329	159	52·2	154	77·3	9·76	20·57	0·337	—	—	—
7·00	3·16	6·27	0·317	152	48·2	141	126	9·92	21·00	0·338	—	—	—
8·00	3·32	7·46	0·359	142	51·0	152	316	9·93	21·40	0·344	—	—	—
9·00	3·83	7·43	0·310	151	46·7	138							

C. Solvent: 80% aqueous alcohol. Temp. 50·0°. Initially [Am$^\gamma$Cl] = 0·1471*N*, and solution neutral. Samples of 10 c.c. titrated. [HCl] expressed in equivalent c.c. of 0·01052*N*-NaOH and [Olefin] in c.c. of 0·04904*N*-$Na_2S_2O_3$.

t (min.).	[HCl].	[Olefin].	E1/(E1+S_N1).	10^6k_1.	10^6k_{E1}.	*t* (min.).	[HCl].	[Olefin].	E1/(E1+S_N1).	10^6k_1.	10^6k_{E1}.
15·00	3·00	5·51	0·428	268	115	85·0	10·81	17·93	0·387	291	113
30·0	5·56	9·58	0·402	282	113	120·0	12·38	20·37	0·383	300	115
45·0	7·52	13·20	0·409	286	117	∞	13·98	—	—	—	—
62·0	9·14	15·98	0·408	285	116						

t (hrs.)	7·0	72·0	167	264	600
[Olefin]	21·61	14·80	9·91	7·83	5·68
E1/(E1 + S_N1)	0·359	0·247	0·166	0·131	0·095
10^3k_H (hrs.$^{-1}$)	—	5·81	4·87	3·95	2·27

The olefin concentrations recorded in the lower half of the table were estimated after the completion of the hydrolysis; the acid concentration remained constant. The reversibility of the hydration is indicated by the downward drift in the value of the pseudo-unimolecular coefficient k_H, calculated from the equation $k_H = \frac{1}{t - t_0} \log_e \frac{a_0}{a_t}$, where a_0 and a_t are the olefin concentrations at t_0 and t respectively (t_0 = 7, and a_0 = 21·61).

D. Solvent: 60% aqueous alcohol. Temp. 25·2°. Initially [Am$^\gamma$Cl] = 0·0783*N*, and solution neutral. Samples of 20 c.c. titrated. [HCl] expressed in equivalent c.c. of 0·1069*N*-NaOH and [Olefin] in equivalent c.c. of 0·050*N*-$Na_2S_2O_3$.

t (min.).	[HCl].	[Olefin].	E1/(E1+S_N1).	10^6k_1.	10^6k_{E1}.	*t* (min.).	[HCl].	[Olefin].	E1/(E1+S_N1).	10^6k_1.	10^6k_{E1}.
7·90	0·92	1·05	0·267	137	36·6	85·40	8·00	8·74	0·256	155	39·6
15·27	1·73	1·92	0·260	137	35·6	120·2	9·81	10·90	0·260	154	40·0
21·85	2·49	2·75	0·258	142	36·7	153·9	10·99	12·15	0·258	151	39·0
33·08	3·68	3·93	0·250	147	36·7	210·0	12·69	13·52	0·249	159	39·7
48·97	5·24	5·79	0·258	150	38·8	∞	14·65	—	—	—	—
64·65	6·54	7·35	0·263	152	40·1						

t (hrs.)	24	265	557	865	1300
[Olefin]	14·61	12·10	10·40	9·10	7·82
E1/(E1+S_N1)	0·233	0·194	0·167	0·146	0·125
10^4k_H (hrs.$^{-1}$)	—	7·83	6·38	5·63	4·90

The acid concentration remained constant in the lower half of the tables; k_H was calculated as in Table III, C (t_0 = 24, a_0 = 14·61).

Hydrolysis of tert.*-Amyl Bromides.*—Two experiments are recorded in Table IV, the cols. of which contain the quantities previously defined.

TABLE IV.

Illustrating determination of first-order rate constants of the hydrolysis of tert.*-amyl bromide.*

A. Solvent: 80% aqueous alcohol. Temp. 25·2°. Initially [Am$^\gamma$Br] = 0·0722*N*, and solution neutral. Samples of 20 c.c. titrated. [HBr] expressed in equivalent c.c. of 0·1069*N*-NaOH and [Olefin] in equivalent c.c. of 0·04906*N*-$Na_2S_2O_3$.

t (min.).	[HBr].	[Olefin].	E1/(E1+S_N1).	10^6k_1.	10^6k_{E1}.	$10^6k_1'$.
3·20	1·40	1·67	0·274	570	156	593
6·50	2·70	3·20	0·272	572	156	593
10·25	4·10	4·59	0·257	589	151	571
14·97	5·50	6·45	0·269	582	157	599
21·30	7·20	8·15	0·260	596	155	584
27·70	8·55	9·49	0·255	604	154	570
36·33	9·90	10·97	0·254	606	154	564
46·13	10·95	12·38	0·259	602	156	579
62·67	11·90	13·31	0·257	567	146	(521)
68·5 hrs.	13·47	15·50	0·264	—	—	—
216 ,,	13·52	14·57	0·248	—	—	—
509 ,,	13·50	14·35	0·244	—	—	—
818 ,,	13·60	13·10	0·222	—	—	—
1154 ,,	13·52	13·25	0·225	—	—	—

B. Solvent: 80% aqueous alcohol. Temp. 25·2°. Initially [Am$^\gamma$Br] = 0·0654*N*, and [NaOH] = 0·1179*N*. [HBr] (as NaOH neutralised) expressed in equivalent c.c. of 0·1564*N*-HCl and [Olefin] in c.c. of 0·04906*N*-$Na_2S_2O_3$.

t (min.).	[HBr].	[Olefin].	E1/(E1+S_N1).	10^6k_1.	10^6k_{E1}.	$10^6k_1'$.
7·90	2·05	4·05	0·310	593	184	595
28·74	5·25	10·57	0·316	572	181	593
38·74	6·17	12·35	0·314	575	183	594
46·10	6·65	13·24	0·312	572	179	587
60·82	7·30	14·33	0·308	564	174	556
140·4	8·11	15·38	0·297	—	—	—
22 hrs.	8·32	15·28	0·288	—	—	—
174 ,,	8·42	16·50	0·307	—	—	—

Hydrolysis of tert.*-Amyl Iodide.*—Olefin estimations could not be carried out during the hydrolysis owing to a reaction between bromine and the *tert.*-amyl iodide (cf. Part II). The rate constants of the total reaction (k_1) were, however, evaluated in acid and in alkaline solution, and the mol.-ratio of olefin to the total decomposition was obtained from estimations made at the end of the reactions. The hydriodic acid concentration in the experiments in initially neutral solution decreased considerably on prolonged standing, owing presumably to oxidation and formation of iodine. Serious error was, however, avoided by carrying out the estimations as soon as possible after the completion of the reaction. The small amount of iodine which was extracted by the carbon tetrachloride was removed by washing with dilute sodium thiosulphate before estimating the olefin. The results are in Table V.

TABLE V.

Illustrating determination of first-order rate constants of the hydrolysis of tert.*-amyl iodide.*

A. Solvent: 80% aqueous alcohol. Temp. 25·2°. Initially [Am$^\gamma$I] = 0·114*N*, and solution neutral. Samples of 5 c.c. titrated. [Am$^\gamma$I] expressed in equivalent c.c. of 0·0526*N*-NaOH.

t (sec.)	116	220	290	358	470	670	932
[Am$^\gamma$I]	8·95	7·49	6·62	5·85	4·78	3·20	1·89
10^5k_1	165	168	170	172	174	182	188

In a similar experiment the acid concentration at the end of the reaction was 0·142*N*, and the olefin values in separate determinations, expressed in c.c. of 0·04904*N*-$Na_2S_2O_3$ per 10 c.c. of reaction mixture, were: 14·85, 15·00, 15·20, 15·04, 14·80.

B. Solvent: 80% aqueous alcohol. Temp. 25·2°. Initially [Am$^\gamma$I = 0·112*N*, and [NaOH] = 0·112*N*. Samples of 5 c.c. titrated. [Am$^\gamma$I] expressed in equivalent c.c. of 0·0782*N*-HCl.

t (sec.)	120	225	310	415	552	718	930
[Am$^\gamma$I]	5·85	4·63	4·14	3·50	2·75	1·96	1·31
10^5k_1	168	194	177	173	173	180	183

In a similar experiment the concentration of *tert.*-amyl iodide was 0·131*N*, and the olefin values at the end of the reaction, expressed in c.c. of 0·04904*N*-$Na_2S_2O_3$ per 10 c.c. of the solution, were: 13·07, 13·15, 13·38, 13·20, 12·92, 13·13, 13·17.

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