

260. *The Mechanism of Elimination Reactions. Part III. Unimolecular Olefin Formation from tert.-Butyl Halides in Acid and Alkaline Aqueous Solutions.*

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The search for unimolecular elimination as an accompaniment of aqueous hydrolysis (this vol., p. 1277) is here extended to *tert.*-butyl chloride, bromide and iodide. The reaction is again found, and its kinetic properties demonstrated.

The prediction that the rates of the unimolecular substitution and elimination should change by much larger factors than their ratio when we pass from one halide to another is again confirmed. From chloride to iodide the individual rates increase by about 100-fold, whilst their ratios remain constant to a factor of 1.3.

As Hughes first showed (J., 1935, 255), the hydrolysis of *tert.*-butyl chloride in aqueous solvents is exclusively unimolecular, even in the presence of alkaline hydroxides; and this result has been generalised by Cooper and Hughes for the other *tert.*-butyl halides (this vol., p. 1183). Since these results indicate that the *tert.*-butyl cation is readily formed, it was of interest to determine whether it would show any tendency, in the presence of the competing attack of a reactive solvent, to break down in the manner which results in the unimolecular production of olefin.

The first point to be determined was whether under any conditions olefin would be formed in sufficient amount for kinetic investigation from *tert.*-butyl halides in aqueous solvents. To our surprise we found that olefin was produced in considerable quantity: the literature had suggested otherwise. In a chemical examination of the products of a completed hydrolysis of *tert.*-butyl chloride Hughes found no olefin (*loc. cit.*); and French, McShan, and Johler, working with *tert.*-butyl bromide in a heterogeneous system, recorded a maximal yield of 2% of olefin (J. Amer. Chem. Soc., 1934, 56, 1346). We now know that there is no inconsistency between these statements and our present finding that about 10—20% of olefin may be formed from these halides: the fact is that under many conditions the olefin, after having been formed comparatively rapidly, disappears again slowly on account of hydration: so that an examination of the products of a "completed" reaction may fail to reveal olefin, or anything like as much of it as has been present; and in order to prove its formation one must follow the variation of its concentration with time from the commencement of the experiment.

We do not elaborate this matter of the eventual disappearance of olefin in the present paper, partly because it is considered more fully in the next paper, which deals with the homologous *tert.*-amyl halides; and partly because, by employing suitable conditions, we were able to study the formation of olefin without serious interference from the subsequent hydration. We show, however, that this hydration of the olefin depends on the development of acidity in the solution, and does not take place in an alkaline medium.

For the study of olefin production we found it convenient generally to employ "80%" aqueous ethyl alcohol as solvent, and the temperature 25°; although some of the experiments on olefin disappearance were, for greater expedition, carried out at 50°.

The occurrence of unimolecular hydrolysis (S_N1) opens up the possibility of unimolecular elimination (E1) for reasons given; but the absence of bimolecular hydrolysis (S_N2), even in alkaline solution, does not imply the exclusion of the independent bimolecular elimination

(E2). We established in the example of *tert.*-butyl bromide that in the presence of a considerable concentration of alkali hydroxide an appreciable part of the olefin-forming process is dependent on the alkali: this part is possibly the bimolecular elimination (E2), although we were unable to isolate it kinetically. The main olefin-producing reaction of both *tert.*-butyl chloride and bromide under all the conditions investigated proceeded by the unimolecular mechanism (E1); its rate was unaffected either by dilute alkali or by acid, and accurately followed the first-order equation. There can be no doubt that olefin formation from *tert.*-butyl iodide is likewise essentially unimolecular, although this halide was not studied in such detail as the others.

The rate of the total reaction, hydrolysis plus elimination ($k_1 = k_{SN1} + k_{E1}$), is interpreted as the rate of formation of the *tert.*-butyl cation. This rate increases in the order chloride < bromide < iodide, by a factor of 44 for the first two, and $2\frac{1}{2}$ for the last two of these halides, for the same solvent and temperature. The ratio of the rate of olefin formation to that of the total reaction for any halide is interpreted as measuring the proportion in which the cation partitions itself between alternative modes of decomposition. Under corresponding conditions, this ratio extends over the range 0.13—0.17 for the same three halides. The figures are as follows:

	$10^5 k_1$.	$10^5 k_{SN1}$.	$10^5 k_{E1}$.	k_{E1}/k_1 .
<i>tert.</i> -Butyl chloride	0.854 sec. ⁻¹	0.710 sec. ⁻¹	0.144 sec. ⁻¹	0.168
" bromide	37.2 "	32.5 "	4.69 "	0.126
" iodide	90.1 * "	78.5 "	11.6 "	0.129

* Cooper and Hughes, *loc. cit.*

The comparatively small variation in the ratio is consistent with the view that the hydrolysis and elimination have a common slow stage (preceding paper).

EXPERIMENTAL.

Methods.—The "80%" aqueous ethyl alcohol used in these experiments was part of a batch employed by Cooper and Hughes (*loc. cit.*), so that our rates at 25° should be directly comparable with theirs. The "80%" alcohol used at an earlier date by Hughes (*loc. cit.*) gave rates about 7% greater, and was presumably very slightly more aqueous (a difference of composition amounting to a small fraction of 1% would account for this difference of rate).

The runs were followed by enclosing samples of the original solution in sealed bulbs, which eventually were broken under carbon tetrachloride, the olefin being extracted with this solvent, and estimated bromometrically as described in the preceding paper. In order to eliminate error due to the formation of olefin before the mixtures, which were sealed up at 0°, had reached the temperature of the thermostat, an "initial" estimation of olefin was made on a sample which had been shaken in the thermostat for one minute. The samples used for the other estimations were similarly shaken in the thermostat for one minute, the end of which was taken as the zero of time.

Because the total reaction and its separate constituents are all of the first order, the constants calculated from the expression $(2.303/t) \cdot \log_{10}\{(x_\infty - x_t)/(x_\infty - x_0)\}$, where the x 's represent olefin concentrations, are rate-constants (k_1) of the total reaction, and not those (k_{E1}) of the partial reaction which actually is being followed analytically. In order to obtain the latter rate-constant we must multiply the former by the proportion of olefin formed. For the purpose of measuring this proportion it is necessary to know something about the rate of disappearance of olefin, in order to ensure that the measurement is not disturbed by this phenomenon.

tert.-Butyl Chloride.—Solvent "80%" aqueous ethyl alcohol throughout.

(Expt. 1). Temp. 25°. Solution originally neutral. Chloride originally about 0.091*M*. Olefin concentrations, x , expressed in c.c. of 1.050*N*/20-thiosulphate per 20 c.c. sample.

t (hours) ...	0.00	6.95	10.00	15.13	21.0	27.0	33.0	"∞"
x (c.c.)	1.45	4.54	5.13	6.98	8.20	9.69	11.26	16.06
k_1 (hr. ⁻¹) ...	—	0.0342	0.0290	0.0317	0.0295	0.0308	0.0337	Mean: 0.0315

(Expt. 2). Temp. 25°. Solution originally 0.10*N* with respect to sodium hydroxide and about 0.091*M* with respect to chloride. Olefin concentrations in c.c. of 0.9745*N*/20-thiosulphate per 20 c.c. sample.

t (hours)	0.00	6.95	10.02	15.58	21.10	27.85	32.4	49.1	"∞"
x (c.c.) ...	0.64	3.05	4.10	6.04	7.05	8.58	9.21	11.43	14.56
k_1 (hr. ⁻¹) ...	—	0.0274	0.0284	0.0316	0.0293	0.0320	0.0295	0.0320	Mean: 0.0300

Summary. Mean k_1 from expts. 1 and 2 = $0.0307 \text{ hour}^{-1} = 0.854 \times 10^{-5} \text{ sec.}^{-1}$. The value obtained by Hughes (*loc. cit.*) by direct measurement of the total reaction was $0.914 \times 10^{-5} \text{ sec.}^{-1}$ (see below).

(Expt. 3). Temp. 25° . Solution originally neutral. Chloride originally $0.182M$. Olefin concentrations in c.c. of $0.9745N/20$ -thiosulphate per 20 c.c. sample. Series of "infinity" values:

t (hours)	120	128	148	168	
x (c.c.)	23.89	23.19	23.72	23.51	Mean: 23.58

(Expt. 4). Temp. 25° . Solution originally neutral. Chloride originally $0.182M$. Olefin concentrations in c.c. of $0.983N/20$ -thiosulphate per 20 c.c. sample. "Infinity" values showing incursion of the olefin hydration:

t (hours)	160	164	168	240	504
x (c.c.)	24.79	24.34	24.04	22.22	17.73

(Expt. 5). Temp. 25° . Solution originally neutral. Chloride originally $0.182M$. Olefin concentrations, x , in c.c. of $0.986N/20$ -thiosulphate, and acidity, y , in c.c. of $1.020N/10$ -alkali, each per 20 c.c. sample. "Infinity" values showing incursion of olefin hydration (x finally falls, whilst y remains constant):

t (hours)	22.6	44.6	71.0	92.3	113.1	160.0	185.0	210.0	240.5
x (c.c.)	13.4	19.44	23.78	25.56	26.86	26.27	25.71	23.7	22.0
y (c.c.)	18.39	—	31.70	33.51	34.17	—	35.25	35.16	34.94

Summary. Proportion of olefin from x_∞ values of expts. 3—5: (3) 0.158, (4) 0.167, (5) 0.180. Mean: 0.168.

(Expt. 6). Temp. 50° . Solution originally neutral. Chloride originally $0.182M$. Olefin concentrations, x , expressed in c.c. of $0.986N/20$ -thiosulphate per 20 c.c. sample. Acidity, y , expressed in c.c. of $1.020N/20$ -alkali. Series showing the incursion of olefin hydration (x finally falls, whilst y remains constant):

t (hours)	0.00	0.32	1.02	2.00	5.20	22.0	47.5	72.4	146.1
x (c.c.)	0.30	7.32	19.26	27.46	31.80	19.52	10.92	6.51	2.28
y (c.c.)	0.33	6.70	19.58	27.70	34.62	—	35.09	35.20	34.56

(Expt. 7). Temp. 50° . Solution originally $0.240N$ with respect to sodium hydroxide. Chloride originally $0.182M$. Olefin concentrations, x , expressed in c.c. of $0.986N/20$ -thiosulphate and alkalinity, z , in c.c. of $0.960N/20$ -acid, each per 10 c.c. sample. Series showing the absence of olefin hydration in alkaline solution.

t (hours)	5.30	25.75	72.3	149.0
x (c.c.)	19.34	19.58	19.46	19.39
z (c.c.)	14.80	13.45	12.72	—

The slow diminution in the value of z probably represents attack by the alkali on the glass of the sealed vessels.

tert.-Butyl Bromide.—Solvent: "80%" aqueous ethyl alcohol; temp. 25° , throughout.

(Expt. 11). Solution originally neutral. Bromide originally $0.0865M$. Olefin concentrations, x , expressed in c.c. of $0.9745N/20$ -thiosulphate per 20 c.c. sample.

t (min.)	0.0	10.0	45.0	72.0	∞			
x (c.c.)	1.75	3.09	6.03	7.49	8.62	8.87	8.51	Mean: 8.67
k_1 (min. $^{-1}$)	—	0.0215	0.0214	0.0245	Mean: $0.0225 = 37.5 \times 10^{-5} \text{ sec.}^{-1}$			

The "infinity" analyses were made between 10 and 20 hours from the commencement of reaction. Olefin hydration remains inappreciable for the first 50 hours (see expt. 15).

(Expt. 12). Solution originally neutral. Bromide originally $0.173M$. Olefin concentrations expressed in c.c. of $0.9745N/10$ -thiosulphate per 20 c.c. sample.

t (min.)	0.0	10.0	24.5	41.1	74.0	" ∞ "
x (c.c.)	0.00	1.74	3.67	5.73	7.42	9.18
k_1 (min. $^{-1}$)	—	0.0210	0.0208	0.0239	0.0244	Mean: $0.0220 = 36.7 \times 10^{-5} \text{ sec.}^{-1}$

(Expt. 13). Solution originally neutral. Bromide originally $0.173M$. Olefin concentration expressed in c.c. of $0.9745N/20$ -thiosulphate per 20 c.c. sample.

t (min.)	0.0	10.1	23.5	42.7	73.1	" ∞ "
x (c.c.)	1.66	5.20	8.30	11.73	14.44	18.00
k_1 (min. $^{-1}$)	—	0.0242	0.0222	0.0224	0.0209	Mean: $0.0224 = 37.3 \times 10^{-5} \text{ sec.}^{-1}$

Summary. Mean k_1 from expts. 11—13 : 37.2×10^{-5} sec.⁻¹. Value obtained by direct measurement of the total reaction (Cooper and Hughes) : 37.4×10^{-5} sec.⁻¹.

(Expt. 14). Solution originally neutral. Bromide originally 0.173*M*. Olefin concentrations in c.c. of 0.983*N*/20-thiosulphate per 20 c.c. sample. Series of "infinity" determinations prior to appreciable olefin hydration.

<i>t</i> (hours)	16	18	20	22	24	
<i>x</i> (c.c.)	17.46	18.27	18.23	17.05	17.24	Mean : 17.65

(Expt. 15). Solution originally neutral. Bromide originally 0.173*M*. Olefin concentrations in c.c. of 0.983*N*/20- or 0.986*N*/20-thiosulphate (*A* or *B* respectively). Readings made with *B* are converted for comparison into terms of *A*. Some values of x_∞ are calculated from measured values of x_t by dividing by the proportion in which the total decomposition of the halide, as determined by measurement of acidity, is incomplete. The purpose of the run is to measure x_∞ , and illustrate the incursion of olefin hydration.

<i>t</i> (hours)	0.00	1.23	3.0	10.7	16.6	57.2	91.5	140.5	312.0
x { c.c. <i>A</i>	2.74	14.00	17.02	—	—	17.94	—	—	—
c.c. <i>B</i>	—	—	—	17.25	17.40	—	16.38	15.88	13.45
% Acidity	—	80.0	98.0	100.0	100.0	100.0	100.0	100.0	100.0
x_∞ , c.c. <i>A</i>	—	17.50	17.36	17.31	17.46	17.94	16.44	15.94	13.49

Mean of 1st five x_∞ values = 17.51 c.c.

(Expt. 16). Solution originally 0.255*N* with respect to potassium hydroxide and 0.173*M* with respect to bromide. Olefin concentrations in c.c. of 0.983*N*/20-thiosulphate for 20 c.c. sample.

<i>t</i> (hours)	16	18	22	24	
<i>x</i> (c.c.)	25.58	25.57	25.60	26.24	Mean : 25.75

Summary. Proportion of olefin from x_∞ values of expts. 11—15 : (11) 0.122, (12) 0.129, (13) 0.127, (14) 0.125, (15) 0.125. Mean : 0.126.

tert.-Butyl Iodide.—Solvent "80%" aqueous ethyl alcohol. Temp. 25° throughout. Accurate time-runs could not be carried out because bromine attacks *tert.*-butyl iodide liberating iodine, thus creating errors of the order of 10% in the estimates of olefin made by the bromination method. Direct estimates of x_∞ are not subject to this error, because *tert.*-butyl iodide is absent from the samples analysed.

(Expt. 21). Solution originally neutral and 0.165*M* with respect to iodide. Olefin concentrations expressed (below) in c.c. of 1.050*N*/20-thiosulphate per 20 c.c. sample.

(Expt. 22). Solution originally neutral and 0.0825*M* with respect to iodide. Olefin concentrations expressed as above.

	Expt. 21.				Expt. 22.		
<i>t</i> (hours)	16	20	24	Mean	16	24	Mean
<i>x</i> (c.c.)	16.04	13.37	17.44	15.6	7.89	7.97	7.93

Summary. Proportions of olefin from x_∞ values of expts. 21 and 22 : (21) 0.129, (22) 0.131. Mean : 0.130.