416. *Mechanism of Elimination Reactions. Part VI. Introduction to a Group of Papers. Unimolecular Olefin Formation from* tert.*-Butyl- and* tert.*-Amyl-sulphonium Salts.*

By K. A. Cooper, E. D. Hughes, C. K. Ingold, and B. J. MacNulty.

The plan on which the present papers are arranged is explained. Part VI is concerned with an extension of the range of examples over which the unimolecular mechanism *E*1 of elimination is kinetically demonstrated. Parts VII and VIII extend the study, initiated in Part V (1940), of environmental factors on the bimolecular and unimolecular mechanisms of elimination, *E*2 and *E*1. Parts IX—XVI deal with constitutional factors, a general discussion of which is given in Part XVI.

The mechanisms *E*1 and S_N1 have a common slow stage in which a carbonium ion $\overset{+}{R}$ is formed. It follows that the proportion in which compounds of a series RX, with constant R and variable X, should suffer substitution and elimination by these mechanisms under similar external conditions, should in first approximation be independent of X. In extension of previous work (Parts II—IV), this is verified for R = *tert.*-butyl and for R = *tert.*-amyl, in each case over the range X = Cl, Br, I, $\overset{+}{S}Me_2$. In the series R = *tert.*-amyl two simultaneous reactions *E*1 occur, producing isomeric olefins. Their proportions should in first approximation be independent of X, and this is confirmed for X = Br, $\overset{+}{S}Me_2$.

INTRODUCTION TO A GROUP OF PAPERS.

WE here indicate the arrangement of the papers of the present running group, and the directions in which they carry forward the various aspects of the general theme with which the series deals. The first three of these papers constitute additions to branches of the subject that have been treated at some length previously. All the rest belong closely together, and are concerned with the development of an aspect which has hitherto been treated only very incompletely. A short preliminary account of the work was given some years ago (*Trans. Faraday Soc.*, 1941, **37**, 657).

The bimolecular mechanism of elimination (*E*2) was first established as a general mechanism by Hanhart and Ingold in 1927. It was subsequently given a certain amount of kinetic foundation, and this the present group of papers considerably extends. We write the mechanism thus,

$$Y + \overset{\curvearrowright}{H{-}CR_2{-}}CR_2\overset{\curvearrowright}{-X} \longrightarrow YH + CR_2{=}CR_2 + X \quad . \quad . \quad . \quad . \quad . \quad (E2)$$

introducing the arrows to show the direction of the electron-transfers, but omitting charge-labels in order to imply inclusion of the various possibilities.

The existence of the unimolecular mechanism of elimination (*E*1) was first pointed out by Hughes in 1935. It is formulated thus,

$$\left.\begin{array}{r} CHR_2{\cdot}CR_2\overset{\curvearrowright}{-X} \xrightarrow[\text{slow}]{} CHR_2{\cdot}\overset{+}{C}R_2 + X \\ Y + \overset{\curvearrowright}{H{-}CR_2{-}}\overset{+}{C}R_2 \xrightarrow[\text{fast}]{} YH + CR_2{=}CR_2 \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (E1)$$

Once again the charges on X and Y are not indicated as there are various possibilities.

The establishment of this mechanism (*E*1) by kinetic methods was the first task to be taken up when the present series of papers was commenced in 1937. Parts I—IV were concerned with this matter, and the present paper, Part VI, provides an addition to that phase of the general inquiry. We here extend to the reactions of sulphonium salts the use of a method, which in the earlier contributions was applied only to alkyl halides, for confirming the unimolecular mechanism of elimination by the study of product-compositions in kinetically controlled conditions. The generality of the unimolecular mechanism of elimination is kinetically demonstrated over a large range of examples in the other papers of the present group.

Part V of the series, published in 1940, was concerned with various factors which control the facility and relative importance of the bimolecular and unimolecular mechanisms of elimination. It dealt chiefly with what were called environmental factors—reagent, concentration, solvent, and temperature. The next two papers of the present group, Parts VII and VIII of the series, continue this study, inasmuch as they add something to our knowledge of solvent and temperature effects on the two elimination mechanisms.

Our main effort in recent years has, however, been devoted to another branch of the subject, *viz.*, the study of constitutional influences, which, as a matter of fact, was just introduced in Part V. All the remaining papers of the present group develop this theme. Parts IX—XV record various experimental contributions. The main results are brought together, and their theoretical interpretation is considered in Part XVI (this vol., p. 2093).

UNIMOLECULAR OLEFIN FORMATION FROM *tert.*-BUTYL- AND *tert.*-AMYL-SULPHONIUM SALTS.

In Part II (*J.*, 1937, 1277) a test of the unimolecular mechanism of elimination, *E*1, was developed on a basis of comparison with the unimolecular mechanism of substitution, S_N1 :

$$\left.\begin{array}{r} CHR_2{\cdot}CR_2\overset{\curvearrowright}{-X} \xrightarrow[\text{slow}]{} CHR_2{\cdot}\overset{+}{C}R_2 + X \\ CHR_2{\cdot}\overset{+}{C}R_2 + Y \xrightarrow[\text{fast}]{} CHR_2{\cdot}CR_2Y \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (S_N1)$$

The two mechanisms, *E*1 and S_N1, are seen to have a common slow stage. The rapid stages of the two mechanisms differ, but both are reactions of the carbonium ion, from which the group X has been removed. Therefore if we operate with a series of compounds RX′, RX″, . . ., containing the same R but a variable X, the specific rate of the total unimolecular reaction

$$k_{\text{heterolysis}} = k_1 = k_{S_N1} + k_{E1}$$

might vary quite largely, but the proportion, k_{E1}/k_1, in which the carbonium ion will decompose in a particular direction should be independent of the nature of X. This is a simplifying over-statement: for stereochemical studies on unimolecular substitution have shown (Cowdrey, Hughes, Ingold, Masterman, and Scott, *J.*, 1937, 1257) that, although X must have passed beyond the separation corresponding to the transition state of heterolysis when the fate of $\overset{+}{\mathrm{R}}$ is determined, it may not be actually very far away, and therefore could have some influence on the relative rates of the alternative decompositions of $\overset{+}{\mathrm{R}}$. However, this effect would be expected to lead to only minor variations in the ratio k_{E1}/k_1, and should certainly not change its order of magnitude; whereas a suitable variation of X might change even the orders of magnitude of the individual rates k_1, k_{S_N1}, and k_{E1}.

The original application of this test, possibly not a very critical one, was to 2-*n*-octyl chloride and bromide, which undergo unimolecular solvolysis in " 60% " aqueous alcohol, giving in part the substitution products, 2-*n*-octyl alcohol and ethyl 2-*n*-octyl ether, and in part the elimination product, octylene. The specific rates of the total solvolytic processes differ by a factor of about 30, but the proportions in which octylene is formed from these two compounds, under the same conditions of solvent and temperature, are the same to within a factor of 1·1. The specific rates of solvolysis were interpreted as the heterolytic rates, k_1, and the olefin proportion as the partition ratio, k_{E1}/k_1, for the decomposition of the separated carbonium ion.

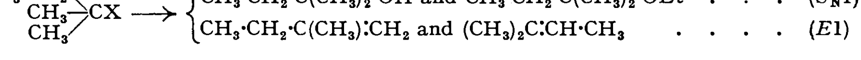
In Part III (*J.*, 1937, 1280) the same test was applied to the unimolecular solvolysis of the *tert.*-butyl halides. In dilute alkaline, neutral and acidic, " 80% " aqueous alcohol, *tert.*-butyl chloride, bromide, and iodide undergo first order reactions, which are in part substitution and in part elimination:

$$(\mathrm{CH_3})_3\mathrm{CX} \longrightarrow \begin{cases} (\mathrm{CH_3})_3\mathrm{C{\cdot}OH} \text{ and } (\mathrm{CH_3})_3\mathrm{C{\cdot}OEt} \quad . \; . \; . \; . \; . \; . \quad (S_N1) \\ (\mathrm{CH_3})_2\mathrm{C{:}CH_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (E1) \end{cases}$$

For this range of substances (X = Cl, Br, I) the specific rates of solvolysis differ by more than 100-fold, but the proportion of olefin remains the same to within a factor of 1·3.

In the same media, dimethyl-*tert.*-butylsulphonium salts also undergo first order solvolytic reactions, which are in part substitution and in part elimination (above formulæ with X = $\overset{+}{\mathrm{S}}\mathrm{Me_2}$). A direct comparison of the solvolysis rates and product compositions for the reactions of *tert.*-butyl chloride and dimethyl-*tert.*-butylsulphonium chloride under identical conditions has now been carried out. The former series RX (with R = $\mathrm{Bu^t}$) has thus been extended to include the sulphonium ion (X = $\overset{+}{\mathrm{S}}\mathrm{Me_2}$, Cl, Br, I), with the result that the rates at a common temperature now vary over a range of 1000-fold, whilst the olefin proportions still remain the same to within a factor of 1·3.

In Part IV (*J.*, 1937, 283) the same method was applied to *tert.*-amyl chloride, bromide, and iodide. In dilute alkaline, neutral, and acidic " 80% " aqueous alcohol, these halides also undergo a first order solvolysis, which is in part a substitution and in part an elimination:



$$\begin{matrix}\mathrm{CH_3{\cdot}CH_2} \\ \mathrm{CH_3} \\ \mathrm{CH_3}\end{matrix}\!\!>\!\mathrm{CX} \longrightarrow \begin{cases} \mathrm{CH_3{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}OH} \text{ and } \mathrm{CH_3{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}OEt} \quad . \; . \; . \quad (S_N1) \\ \mathrm{CH_3{\cdot}CH_2{\cdot}C(CH_3){:}CH_2} \text{ and } \mathrm{(CH_3)_2C{:}CH{\cdot}CH_3} \quad . \; . \; . \; . \quad (E1) \end{cases}$$

Here again the solvolysis rates are changed by large factors, whilst the proportions of (total) olefin remain nearly constant.

For the same media, an analogous first-order solvolysis is undergone by dimethyl-*tert.*-amylsulphonium chloride (above formulæ with X = $\overset{+}{\mathrm{S}}\mathrm{Me_2}$). Accordingly, a comparison has been made of the total solvolysis rates, and of the proportions of total olefin, for the reactions of *tert.*-amyl chloride and dimethyl-*tert.*-amylsulphonium chloride under identical conditions. Thus the previous series RX (with R = *tert.*-amyl) has been extended to include the sulphonium ion (X = $\overset{+}{\mathrm{S}}\mathrm{Me_2}$, Cl, Br, I), with the result that the rates at a common temperature vary in the extended series over a range of about 500-fold, whilst the olefin proportions remain the same to within a factor of 1·5.

All the above results are included in Table I. They are interpreted as meaning that the solvolytic formation of olefin from the dimethyl-*tert.*-butyl- and -*tert.*-amylsulphonium ion under the conditions mentioned proceeds by the unimolecular elimination mechanism *E*1, just as it does in the analogous reactions of the *tert.*-butyl and *tert.*-amyl halides.

TABLE I.

Effect of variation of X *on the rate-constant* k_1 (*sec.*$^{-1}$) *and on the rate-ratio* k_{E1}/k_1 *in unimolecular decomposition of* RX.

Solvent.*	Temp.	R.	X.	10^5k_1.	k_{E1}/k_1.	Ref.
60% EtOH	100·0°	2-*n*-Octyl	Cl	0·805	0·13	Part II
			Br	26·8	0·14	
80% EtOH	25·0	*tert.*-Butyl	Cl	0·854	0·168	Part III
			Br	37·2	0·126	
			I	90·1	0·129	
,,	65·3	,,	Cl	89·7	0·363	This paper
			$\overset{+}{\mathrm{S}}\mathrm{Me}_2$	11·8	0·357	
,,	25·2	*tert.*-Amyl	Cl	1·50	0·333	Part IV
			Br	58·3	0·262	
			I	174	0·260	
,,	50·0	,,	Cl	28·5	0·403	This paper
			$\overset{+}{\mathrm{S}}\mathrm{Me}_2$	6·66	0·478	

* "*x*% EtOH" means a mixture made from *x* vols. of ethyl alcohol and (100 − *x*) vols. of water.

In the case of the *tert.*-amyl compounds another test of mechanism, similar in general principle to that just described, can be based on the fact that the amylenes produced are mixtures of isomerides. For if they arise by decomposition of a separated carbonium ion, then the proportions in which the isomerides are formed should be nearly independent of the molecule from which the carbonium ion is derived. The necessary comparison of the compositions of the olefin mixtures has been made for those olefins which are formed by unimolecular solvolysis of *tert.*-amyl bromide and dimethyl-*tert.*-amylsulphonium iodide in anhydrous, or nearly anhydrous ethyl alcohol. The determinations were made in connexion with other work, and experimental details will be found in Parts XI and XIV; but those results which are relevant to the present question are cited in Table II. The olefin compositions differ by little more than the experimental error, and their similarity confirms the unimolecular nature of the reactions in which the olefins are formed.

TABLE II.

Effect of variation of X *on the composition of olefin mixtures formed by the decomposition of* RX.

Solvent.	Temp.	R.	X.	$Me_2C{:}CHMe$, %.	$MeEtC{:}CH_2$, %.
100% EtOH.........	25°	*tert.*-Amyl	Br	82	18
97% EtOH.........	24	,,	$\overset{+}{\mathrm{S}}\mathrm{Me}_2$	87	13

EXPERIMENTAL.

Materials.—Dimethyl-*tert.*-butylsulphonium iodide was prepared as described by Hughes and Ingold (*J.*, 1933, 1571). Dimethyl-*tert.*-amylsulphonium iodide was prepared by allowing freshly decolorised and distilled *tert.*-amyl iodide to combine with dimethyl sulphide in concentrated solution in nitromethane at room temperature. It was crystallised from ethyl alcohol (Found : C, 32·0; H, 6·7; I, 48·8. Calc. : C, 32·3; H, 6·5; I, 48·8%). The iodides in aqueous solution were converted into hydroxides by means of silver oxide, and from the hydroxides the chlorides were prepared by neutralisation with hydrochloric acid. The alcohol–water solvents were made up by volume (cf. Table I, footnote).

Method of Kinetic Measurements.—In all cases the runs were followed by enclosing samples of the original solution at 0° in sealed bulbs, which, after suitable intervals of heating in the thermostat, were quickly cooled with ice–water, and either broken under ice–water when it was intended to estimate the total decomposition, or broken under ice-cold carbon tetrachloride when the purpose was to estimate the olefin. Total decomposition was estimated by titrating the liberated acid with standard alkali using phenolphthalein as indicator. The olefin was estimated bromometrically as described below. In order to eliminate errors due to the formation of acid and of olefin before the sealed-up mixtures had reached the temperature of the thermostat, pairs of tubes were shaken for two minutes in the thermostat and then used immediately for " initial " estimations of the acid and olefin. The samples used for other estimations were similarly shaken in the thermostat for two minutes, the end of which period was taken as the time-zero.

Methods for Olefin Estimations.—The general methods, with the modifications needed for particular cases, have been described several times before, the most recent account being contained in Part V (*J.*, 1940, 901). We used the extraction technique, but, in the case of the sulphonium salts, we had to introduce a modification in order to eliminate interference from the produced sulphides. The modification consisted of washing the carbon tetrachloride solution (150 c.c.) twice with ice-cold saturated aqueous mercuric chloride (50 c.c.). This removed the sulphides sufficiently well, and caused no detectable loss of amylenes, as was shown by blank experiments. It did produce appreciable losses of butylene, but these were small and regular enough to be compensated by using blank experiments for standardisation, as described before (*loc. cit.*). As Hughes and MacNulty showed (*J.*, 1937, 1283), olefin which is produced in a solution which is also developing acid, tends in due course to disappear owing to hydration; and thus the apparent proportion in which the total reaction leads to olefin at first remains substantially constant and then begins to decrease. Thus the olefin present at a late stage of a run is not a suitable measure of what has been produced; and, on the other hand, measurements of olefin made early in a run are rendered inaccurate by the smallness of the quantity of olefin. The usual procedure was therefore first to carry out a run in which both the acid and the olefin were estimated throughout its course, and then, having from these results selected the range of times most favourable for accurate olefin measurements, to carry out a second run in which most of the tubes employed for olefin estimations were taken out of the thermostat at just one or two times within the favourable period.

Results of Measurements.—The principal results are summarised in Table I. Details of some illustrative runs are given in Table III.

TABLE III.

Illustrating determinations of first-order rate-constants and the proportions of olefin formed in the solvolysis of alkyl halides and sulphonium salts.

(1) *Dimethyl*-tert.-*butylsulphonium Chloride.*—Solvent: " 80% " ethyl alcohol. Temperature 65·3°. (*a*) [SMe_2Bu^tCl] initially 0·0640M. Solution initially neutral. In this run the first-order development of acid only was followed, leading to $10^5k_1 = 11{\cdot}8$ sec.$^{-1}$. (*b*) [SMe_2Bu^tCl] initially 0·0643M. Solution initially neutral. Olefin *x* expressed in c.c. of 0·0675N-thiosulphate per 20 c.c. sample. Comparison is made with the total reaction as calculated for the different times *t* from the above rate-constant:

t (min.) (corr.)	0·0	20·0	30·0	40·0	50·0	75·0	90·0
x (c.c.) (uncorr.)	2·01	4·42	4·83	5·74	6·46	6·99	8·28
x (c.c.) (corr.)	—	2·41	2·82	3·73	4·45	4·98	6·27
Yield % olefin (corr.)	—	6·3	7·4	9·8	11·65	13·05	16·4
Total reaction %	0·0	13·2	19·2	24·6	34·6	41·2	47·1
Proportion of olefin %	—	(48)	38·5	39·8	33·7	31·7	34·8

(2) tert.-*Butyl Chloride.*—Solvent: "80%" ethyl alcohol. Temperature 65·3°. [Bu^tCl] initially 0·182M. Solution initially neutral. Olefin *x* expressed in c.c. of 0·0682N-thiosulphate, and acidity *y* in c.c. of 0·0771N-alkali, each for a 20 c.c. sample:

t (min.) (corr.)	0·0	20·0	30·0	40·0	50·0	60·0	70·0	934·0
x (c.c.) (uncorr.)	1·60	28·04	32·04	34·59	35·60	36·28	35·55	7·56
y (c.c.) (uncorr.)	1·64	31·89	37·91	—	45·03	45·95	46·44	47·17
Proportion of olefin %	—	38·5	37·6	—	34·6	34·6	33·6	7·0

The figures show that hydration of the *iso*butylene becomes appreciable after the first hour.

(3) *Dimethyl*-tert.-*amylsulphonium Chloride.*—Solvent: " 80% " ethyl alcohol. Temperature 49·9°. [SMe_2Am^tCl] * initially 0·04608M. Solution initially neutral. Olefin, and the bromine by absorption of which it is measured, are reckoned in c.c. of 0·0492N-thiosulphate, and acidity *y* is given in c.c. of 0·0406N-alkali, each for a 10 c.c. sample.

t (min.) (corr.)	20	45	75	110	150	200	270	380
y (corr.)	0·80	1·80	2·95	4·00	5·20	6·30	7·50	8·90
10^5k_1 (k_1 in sec.$^{-1}$)	6·12	6·39	6·68	6·58	6·81	6·75	6·67	6·73

The final reading y_∞ was 11·35 c.c. A series of " initial " tubes gave acid production 0·30 c.c., and residual bromine, after its uptake by olefin, 14·10 c.c. (means). A further set of tubes withdrawn from the thermostat 180 mins. later gave acid 6·20 c.c., and residual bromine 9·40 c.c. (means). The proportion of olefin is therefore 47·8%. The comparison experiments on *tert.*-amyl chloride were included in the paper by Hughes and MacNulty (*loc. cit.*).

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

[*Received, January 15th,* 1948.]

* Am^t = *tert.*-amyl.