259. *The Mechanism of Elimination Reactions. Part II. Unimolecular Olefin Formation from* sec.*-Octyl Halides in Aqueous Alcohol. A New Criterion of Mechanism.*

By Edward D. Hughes, Christopher K. Ingold, and Uriel G. Shapiro.

Unimolecular elimination having been observed in non-aqueous solvents (this vol., p. 1271), it was next sought as accompaniment of unimolecular substitution in the aqueous hydrolysis of secondary and tertiary alkyl halides. In this work β-*n*-octyl chloride and bromide were used. The reaction was found, and its kinetic properties demonstrated.

It follows from the mechanism assumed for unimolecular substitution and elimination that, for the same alkyl group, a change in the halogen atom should have a direct and possibly large effect on the rates of the individual simultaneous reactions, but only an indirect and relatively small effect on the ratio of the rates. Consistently we find, on passing from chloride to bromide, that the rates are increased about 35-fold, whilst the ratio remains constant to within 10%.

Evidence was given in Part I that in certain non-aqueous solvents alkyl halides can yield olefins by a unimolecular mechanism dependent on slow halogen-ionisation followed by the rapid loss of a proton from the unstable cation thus formed :

$$\left.\begin{aligned} \mathrm{CHR_2{\cdot}CR_2{\cdot}Hal} &\xrightarrow{\text{slow}} \mathrm{CHR_2{\cdot}\overset{+}{C}R_2} + \mathrm{\overset{-}{Hal}} \\ \mathrm{CHR_2{\cdot}\overset{+}{C}R_2} &\xrightarrow{\text{fast}} \mathrm{CR_2{:}CR_2} + \mathrm{H^+} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{E1})$$

In this and the immediately following papers we describe a search for the same reaction in aqueous solvents; and we also develop an independent proof of mechanism.

In aqueous, or, more generally, in hydroxylic, solvents there are other ways than the loss of a proton in which the assumed cation can be converted into a stable compound: unimolecular elimination, if it occurs, must be an accompaniment of unimolecular hydrolytic substitution. Unimolecular substitution appears to be general for secondary and tertiary alkyl halides, and it was therefore amongst the reactions of these compounds that we commenced the search for unimolecular elimination. The secondary compounds which we have examined with respect to unimolecular hydrolytic substitution include *iso*propyl and β-*n*-octyl halides, and it is in the case of the latter that we succeeded first in observing simultaneous unimolecular elimination.

The hydrolytic reactions of β-*n*-octyl bromide were examined by Hughes and Shapiro (this vol., p. 1192) in 60% aqueous ethyl alcohol at 80°. In alkaline solution they found a unimolecular substitution (S_N1), and a bimolecular substitution (S_N2), both consisting partly in hydrolysis and partly in alcoholysis, together with a bimolecular olefin elimination (E2). In acid solution the two bimolecular reactions became negligible, leaving the unimolecular substitution (S_N1) in control. Now the progress of this reaction was followed by noting the development of acidity, and hence its measured rate would include that of any simultaneous unimolecular elimination. Our first step, therefore, was to determine whether any of the total first-order reaction actually resulted in the production of olefin; and we found that 10% of it did so. Anticipating the evidence that the olefin thus obtained is actually the product of a unimolecular elimination (E1), we may set down the proportions in which the various reactions take place side by side, either in an acid medium, or in a sensibly constant 0·8*N*-concentration of alkali:

$$\text{Acid—1st Order } 100\%\left<\begin{array}{ll} \mathrm{S_N1} & 90{\cdot}3\% \\ \mathrm{E1} & 9{\cdot}7\% \end{array}\right.$$

$$0{\cdot}8N\text{-Alkali}\left<\begin{array}{l} \text{1st Order } \ 7{\cdot}25\%\left<\begin{array}{ll}\mathrm{S_N1} & 6{\cdot}5\% \\ \mathrm{E1} & 0{\cdot}7\%\end{array}\right. \\ \text{2nd Order } 92{\cdot}75\%\left<\begin{array}{ll}\mathrm{S_N2} & 41{\cdot}7\% \\ \mathrm{E2} & 51{\cdot}1\%\end{array}\right.\end{array}\right. \quad \begin{array}{l}\text{Substitution } 48{\cdot}2\% \\ \text{Elimination } 51{\cdot}8\%\end{array}$$

The rate constants of the four reactions at 80° in the solvent mentioned are as follows:

$\mathrm{S_N1}$ $10^4k_1 = 0{\cdot}466$ sec.$^{-1}$ $\mathrm{S_N2}$ $10^4k_2 = 3{\cdot}58$ sec.$^{-1}$g.-mol.$^{-1}$l.
E1 $10^4k_1 = 0{\cdot}050$ sec.$^{-1}$ E2 $10^4k_2 = 4{\cdot}39$ sec.$^{-1}$g.-mol.$^{-1}$l.

Further experiments have been carried out at 100° in the same solvent, and with β-*n*-octyl chloride as well as the bromide.

It was necessary next to prove that the formation of octylene in acid solution is in fact kinetically of the first order: this cannot be regarded as established by the proved first order of the total reaction, since the elimination is a relatively small part of the complete process. The reaction was therefore followed by estimating, not the acidity or the bromide ions as heretofore, but the olefin, the analysis being carried out by addition of bromine. The logarithms of the olefin concentrations gave linear plots against the time to within the error of analysis, and the rate constants derived as usual from the slopes of the graphs agreed with those deduced from measurements of acidity or of halide ions. Thus, not only is the total reaction of the first order, but so also is its minor constituent, the elimination; and the amount of olefin formed at any time is a constant fraction of the quantity of halide decomposed.

A test of mechanism follows from a comparison of the suggested mechanisms for unimolecular elimination and unimolecular substitution. Both assume the same rate-controlling process, *viz.*, the slow ionisation of the alkyl halide. The postulated rapid steps differ, but they are both assumed to be reactions of the organic cation, the anion not being concerned. It follows that the ratio of the rates with which the cation, when once formed, will decompose in the two possible ways should be independent of the nature of the anion. The reactions may be written:

$$\mathrm{R{\cdot}X} \xrightarrow[\text{(slow)}]{} \overset{+}{\mathrm{R}} + \overset{-}{\mathrm{X}} \left\{ \begin{array}{ll} \overset{+}{\mathrm{R}} \xrightarrow[\mathrm{H_2O}]{} \mathrm{R{\cdot}OH} + \overset{+}{\mathrm{H}} \text{ (fast)} \quad . \quad . \quad . \quad . & (\mathrm{S_N1}) \\ \overset{+}{\mathrm{R}} \longrightarrow \text{Olefin} + \overset{+}{\mathrm{H}} \text{ (fast)} \quad . \quad . \quad . \quad . & (\mathrm{E1}) \end{array}\right.$$

The rate of ionisation of the alkyl halide is the rate of the total first-order decomposition (k_1) :

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

For a given solvent and temperature, the rate k_1, and its components k_{S_N1} and k_{E1}, will in general vary largely from one compound RX to another; in particular they will vary when, with a constant alkyl group R, we modify X. But the proportion in which the first-order reaction follows a particular path, *i.e.*, the ratio k_{E1}/k_1, should depend essentially on R, and not on X. This statement represents only a first approximation, and is too sweeping to be quite accurate : for, as our stereochemical studies have shown, X may be only a few atomic diameters away when the fate of R is determined, and therefore the nature of X may have some small influence on the result. We know that, when, in unimolecular hydrolysis, the dissociation of RX has passed over its energy barrier, the receding X^- still shields R^+ sufficiently to cause a disparity between the rates at which R^+ is attacked from the two sides: there is incomplete racemisation. Therefore X^- may be expected, at the same stage of dissociation, to have an appreciable influence on the relative rates at which R^+ suffers attack in the two possible locations, *viz.*, at the cationic carbon atom and at the β-hydrogen atom. However, this effect would be expected to create only minor variations in the ratio of velocities, and should certainly not affect its order of magnitude; whereas by changing X we might well change even the orders of magnitude of the velocities themselves. On passing from β-*n*-octyl chloride to the bromide the value of k_1 is in fact increased 33-fold, and k_{S_N1} and k_{E1} are increased similarly; but the ratio k_{E1}/k_1 is scarcely altered by 10%. The values for 100° are as follows :

	$10^5 k_1$.	$10^5 k_{S_N1}$.	$10^5 k_{E1}$.	k_{E1}/k_1.
β-*n*-Octyl chloride	0·805 sec.$^{-1}$	0·700 sec.$^{-1}$	0·105 sec.$^{-1}$	0·13
β-*n*-Octyl bromide	26·8 ,,	23·0 ,,	3·75 ,,	0·14

Some further applications of this principle are given in the following papers, and the results are uniformly in favour of the unimolecular mechanisms suggested.

EXPERIMENTAL.

Methods.—An approximately *N*/10-solution containing an accurately known weight of β-*n*-octyl chloride or bromide in an aqueous alcohol prepared from 8 vols. of anhydrous ethyl alcohol and 2 vols. of water was made up; and 5 c.c. portions of this were enclosed, each with a 5 c.c. portion of an aqueous alcohol made from 4 vols. of dry ethyl alcohol and 6 vols. of water, in a series of bulbs, which were warmed and shaken until the contents were homogeneous, and then heated at 80° or 100° for the required length of time. Each bulb was then crushed under 100 c.c. of carbon tetrachloride, and the solution thus obtained was washed with water, and treated for 0·5 hour with a standard solution of bromine, the excess of which was then titrated with *N*/50-thiosulphate. A blank experiment conducted in the same way, but without giving opportunity for the development of olefin, served to standardise the bromine solution.

Results.—These are given in the introduction, but we add some illustrative details. The following record represents a determination (Expt. 171) of the progress of olefin development from β-*n*-octyl chloride in 60% aqueous ethyl alcohol at 100°. The original concentration of chloride in this experiment was 0·0570*M*. Samples of 10 c.c. were used for each estimation of olefin, and the quantity of this found is expressed as its equivalent in c.c. of *N*/50-thiosulphate solution :

Time (hours)	6·0	15·0	22·0	28·0	46·0	∞
Olefin (c.c. of $Na_2S_2O_3$)	1·37	3·12	3·72	3·97	5·24	7·37

The graphically determined rate constant agrees with the mean value given previously. For the chloride at 100° the constants k_1 ranged from $0·99 \times 10^{-5}$ (an isolated high value) to $0·77 \times 10^{-5}$ sec.$^{-1}$; for the bromide at 80° only a single determination was made, and for the bromide at 100° two determinations, which gave $25·5 \times 10^{-5}$ and $28·1 \times 10^{-5}$ sec.$^{-1}$. It will be appreciated that, since the proportion of the total decomposition which yields olefin is constant throughout the unimolecular reaction, the rate constants calculated in the usual way from the slopes of the logarithmic plots of the olefin estimations represent k_1 and not k_{E1}. In order to obtain k_{E1} it is necessary to determine the proportion of the total decomposition which results in olefin, and separate estimates of this quantity gave the following results, the solvent being in all cases 60% aqueous ethyl alcohol.

β-*n*-Octyl bromide at 80°	9·12	9·49	9·59	10·60%
β-*n*-Octyl chloride at 100°	13·1	13·4	12·6	12·7%
β-*n*-Octyl bromide at 100°	14·0	14·1	14·0%	

The means of these figures are quoted in the introduction.

University College, London.

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