420. *Mechanism of Elimination Reactions. Part X. Kinetics of Olefin Elimination from* iso*Propyl,* sec.-*Butyl,* 2-n-*Amyl, and* 3-n-*Amyl Bromides in Acidic and Alkaline Alcoholic Media.*

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Data are recorded to show certain constitutional effects on the rates of the constituent substitutions and eliminations which secondary alkyl bromides undergo in bimolecular reactions with ethoxide ions in anhydrous ethyl alcohol, and also in solvolytic reactions with 60% aqueous ethyl alcohol. Elimination rates are analysed, where possible, into those of the component elimination processes which establish the double bond in alternative branches of the secondary alkyl group. The structural effects studied relate to increases in alkyl chain-length beyond the β-carbon atom in either or both of the branches of the secondary group.

The bimolecular substitution rate drops with ascent of a homologous secondary alkyl series more slowly than it drops in an analogous primary alkyl series; and it drops somewhat more slowly in the secondary series when less concentrated alkali is employed for the reaction. These quantitative differences are ascribed to the operation of mixed mechanisms near the conditions for change to the unimolecular mechanism of substitution. Bimolecular elimination rate is increased by the introduction of β-linked methyl substituents in either or both of the alkyl branches, and is decreased, but less sharply, if such a branch is further lengthened by continued alkyl substitution. Each change of elimination rate from one compound to another is more than accounted for by a change in the rate of establishment of the double bond in the altered alkyl branch, this effect being partly off-set by smaller contrary changes in the rate of entrance of the double bond into the alkyl branches which remain similar. These relations are interpreted in Part XVI.

The solvolytic reactions in neutral and acidic aqueous alcohol consist in part of bimolecular substitution with a solvent molecule as substituting agent, and in part of unimolecular substitution and elimination. Because of the composite molecularity of the total solvolytic substitution, no attempt is made to analyse the obviously complicated structural effects on the solvolytic substitution rate. However, the solvolytic elimination will be wholly unimolecular in mechanism, and its rate should be intelligibly related to structure. It is found that the unimolecular elimination rate is increased by the introduction of a β-linked methyl substituent in either or both of the alkyl branches, and is decreased, but less sharply, if such a branch is further lengthened by continued alkyl substitution. These effects also are interpreted in Part XVI.

THE investigation of constitutional effects on olefin elimination from secondary alkyl halides provides a more complicated problem than did the similar study of primary halides described in the preceding paper. For this there are several reasons.

One is that in secondary alkyl halides the tendency towards bimolecular and unimolecular reactions of substitution and elimination are all developed to an appreciable extent. Therefore, in general, at least four reactions, those to which we give the type-labels S_N2, $E2$, S_N1, and $E1$, require to be kinetically separated, and individually studied with respect to constitutional influences.

Of these four processes, the two bimolecular reactions, S_N2 and $E2$, can readily be examined, without serious interference from the unimolecular reactions, by the use of a somewhat weakly ionising solvent, such as anhydrous ethyl alcohol, and moderately large concentrations of strongly basic reagents, such as hydroxide or ethoxide ion. On the other hand, even in alcohol–water mixtures of marked ionising character, the tendency shown by secondary alkyl halides to undergo the unimolecular reactions S_N1 and $E1$ is not usually so great that these processes can be kinetically isolated from the bimolecular reactions in the presence of conveniently measurable concentrations of alkali. One is therefore compelled to pursue the kinetic study of the unimolecular reactions in nearly neutral and acidic solutions, thereby introducing the well-known difficulty, peculiar to solvolytic processes, of distinguishing between true unimolecular reactions involving the prior ionisation of the alkyl halide, and bimolecular reactions in which the solvent molecule is the reagent. These two types of reaction may both exhibit accurate or approximate first-order kinetics, and therefore the distinction between them usually has to depend on indirect evidence of various kinds.

The remaining general point concerning secondary alkyl halides is that some of them are so constituted that different olefins can be formed from them by elimination along different branches of the alkyl structure. It follows that the set of simultaneous reactions requiring separate measurement in a given case, and comparison from case to case, may include two concurrent eliminations of either kinetic type.

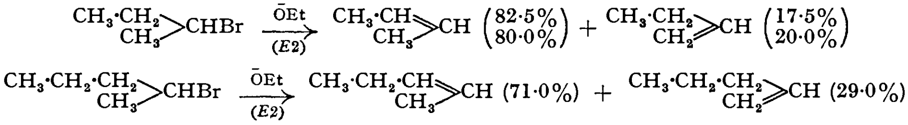
The following alkyl halides have been included in the present study : *iso*propyl, *sec.*-butyl, 2-*n*-amyl, and 3-*n*-amyl bromide. The first and fourth of these can each give rise to only one olefin, whilst the second and third can, and do, each produce a mixture of two isomeric olefins (three, allowing for the geometrically isomeric forms of one of the position isomerides). The examples are chosen in order to provide two series, one of which illustrates the effects of progressive homology through the lengthening of a chain, whilst the other exemplifies the effect of the introduction of successive β-linked methyl groups: Series 1: $CH_3(CHMeBr)$, $CH_3{\cdot}CH_2(CHMeBr)$, $CH_3{\cdot}CH_2{\cdot}CH_2(CHMeBr)$. Series 2: $Me_2(CHBr)$, $MeEt(CHBr)$, $Et_2(CHBr)$.

There are several relevant previous investigations. The set of simultaneous substitutions and eliminations undergone by *iso*propyl bromide under various conditions of alkalinity were kinetically analysed by Hughes, Ingold, and Shapiro (*J.*, 1936, 225). They employed two solvents, " 60% " aqueous ethyl alcohol (a mixture of 3 vols. of ethyl alcohol and 2 vols. of water) and " 80% " ethyl alcohol (4 vols. of alcohol plus 1 vol. of water), and a range of temperatures. Hughes, Ingold, Masterman, and MacNulty (*J.*, 1940, 899) extended the work, employing anhydrous ethyl alcohol as solvent, and a wide range of ionic strengths, but only one temperature, this being chosen for its suitability in the comparison of typical primary, secondary, and tertiary alkyl halides having very different kinds of reactivity. An investigation of olefin elimination from 2-*n*-butyl and 2-*n*-amyl bromide has been carried out by Lucas and his collaborators (Lucas, Simpson, and Carter, *J. Amer. Chem. Soc.*, 1925, **47**, 1462; Lucas, Dillon, and Young, *ibid.*, 1930, **52**, 1949). Without making any kinetic measurements on the processes studied, these authors carried out some careful determinations of the compositions of the mixtures of isomeric olefins which are formed from each halide by the action of hot ethyl-alcoholic potassium hydroxide.

In the present work, anhydrous ethyl alcohol has been used for the investigation of the bimolecular processes, and " 60% " aqueous ethyl alcohol for that of the unimolecular reactions. The bimolecular reactions in dry ethyl alcohol have been studied under two sets of conditions. In the first, the reagent was 4N-potassium hydroxide, and the temperature 80·0°, these conditions being chosen in order that the kinetic results could be correlated with the above-mentioned analytical work of Lucas and his collaborators. However, although the reaction rates could be measured in these conditions, the reactions were rather too fast for accurate kinetic study by our methods. Furthermore, the reagent is not as simple as it could be, since the entity which attacks the alkyl halide molecules, though it probably consists mainly of ethoxide ions, must actually be a mixture of hydroxide and ethoxide ions. We have therefore endeavoured to secure a series of more accurate, and possibly more simply interpretable, kinetic data by means of a parallel series of measurements under a second set of conditions, in which the reagent was 1N-sodium ethoxide and the temperature 25·0°, the solvent being dry ethyl alcohol as before.

It can be shown that, in the presence of 4N-potassium hydroxide in dry ethyl alcohol at 80°, the total reaction is substantially bimolecular: the incursion of first-order processes amounts to less than 1%, and is therefore negligible. We are thus dealing essentially with the substitution and elimination processes S_N2 and $E2$. Just as in the corresponding study with primary halides (Part IX), two types of measurement were made in each example. First, we measured the total bimolecular rate constant, k_2, by following the liberation of halide ion. Then we determined the proportion in which the total reaction yields olefin, and on that basis split up the over-all constant, k_2, into its component parts, $k(S_N2)$ and $k(E2)$, relating to the substitution and elimination. Since the solutions are alkaline, olefin, when once formed, is not destroyed, and hence the proportion in which it is produced can conveniently be estimated at the conclusion of reaction.

In those cases in which the elimination constant, $k(E2)$, is itself composite, owing to the simultaneous formation of isomeric olefins, this constant can be split into its components with the help of Lucas's analytical data. These are given in the following scheme, if one reads the upper line of figures entered against the butylenes. Lucas's analysis of the mixture of butylenes has been repeated by Dr. L. I. Woolf, as described in Part XIII. His results are summarised in the lower line of figures given for the butylenes. We use the mean of Lucas's and Woolf's results in our analyses of the elimination rate-constants, $k(E2)$:



$$\begin{matrix}CH_3{\cdot}CH_2\\CH_3\end{matrix}\!>\!CHBr \xrightarrow[(E2)]{\bar{O}Et} \begin{matrix}CH_3{\cdot}CH\\CH_3\end{matrix}\!\gg\!CH \begin{pmatrix}82{\cdot}5\%\\80{\cdot}0\%\end{pmatrix} + \begin{matrix}CH_3{\cdot}CH_2\\CH_2\end{matrix}\!\gg\!CH \begin{pmatrix}17{\cdot}5\%\\20{\cdot}0\%\end{pmatrix}$$

$$\begin{matrix}CH_3{\cdot}CH_2{\cdot}CH_2\\CH_3\end{matrix}\!>\!CHBr \xrightarrow[(E2)]{\bar{O}Et} \begin{matrix}CH_3{\cdot}CH_2{\cdot}CH\\CH_3\end{matrix}\!\gg\!CH\ (71{\cdot}0\%) + \begin{matrix}CH_3{\cdot}CH_2{\cdot}CH_2\\CH_2\end{matrix}\!\gg\!CH\ (29{\cdot}0\%)$$

Lucas and his co-workers were unable to determine the proportion in which the but-2-ene is composed of *cis*- and *trans*-isomerides. According to Woolf, the but-2-ene consists almost entirely of the *cis*-compound.

In the presence of 1N-sodium ethoxide in anhydrous ethyl alcohol at 25°, the total reaction is still substantially bimolecular although the incursion of first-order processes may amount to 2 or even 3%. We still treat the reaction as containing essentially only the processes S_N2 and $E2$, and, as before, determine the total bimolecular rate-constant, and the olefin proportion, in each example. We have analysed the results as before, even to the stage in which Lucas's and Woolf's results are employed, since the kinetic constants are certainly more accurate, and we think that Lucas's and Woolf's olefin compositions will apply under the changed conditions to quite a good approximation, perhaps to within the limits of the errors in the measurements themselves (cf. Part XIV).

Table I contains the observational data for both the sets of conditions specified. In Table II these data are analysed in the manner described. The figures are arranged to show the effects arising from the two types of progressive structural change which our compounds illustrate.

TABLE I.

Second-order rate-constants (k_2 *in sec.*$^{-1}$ *g.-mol.*$^{-1}$ *l.*), *and percentages of olefin formed, in the reactions of secondary alkyl bromides with potassium hydroxide and with sodium ethoxide in anhydrous ethyl alcohol.*

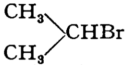
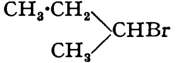
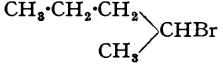
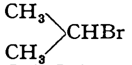
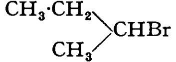
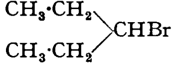
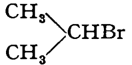
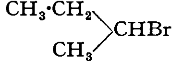
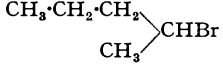
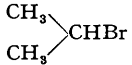
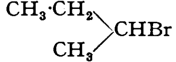
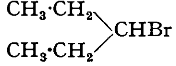
Conditions.	Alkyl bromide.	10^5k_2.	% Olefin.	
			Determinations.	Mean.
4N-KOH at 80·0°	2-Propyl	162	88·0, 86·2	87·1
	2-*n*-Butyl	209	90·0, 92·8	91·4
	2-*n*-Amyl	165	91·6, 89·2	90·4
	3-*n*-Amyl	211	96·0, 97·7	96·8
1N-NaOEt at 25·0°	2-Propyl	0·295	82·7, 78·0	80·3
	2-*n*-Butyl	0·422	82·3, 79·7, 84·6	82·2
	2-*n*-Amyl	0·343	79·4, 82·0	80·7
	3-*n*-Amyl	0·454, 0·455	87·5, 88·6	88·1

We shall comment here only on the substitution rates, since the elimination rates will be comprehensively considered later and in Part XVI. Since the olefin estimations admit of possible errors up to 3% (cf. Hughes, Ingold, Masterman, and MacNulty, *loc. cit.*), the figures $10^5k(S_N2)$ given in Table II for the reactions with 4N-potassium hydroxide are liable to errors up to 5 units, whilst the corresponding figures for the reactions with 1N-sodium ethoxide involve possible errors of 0·01. In the former case it would seem that a fall of rate accompanies ascent of the homologous series, though the details are obscured by the experimental error. In the latter, all that can be said is that the values show no marked trend in either direction.

We interpret these facts, as similar phenomena have been interpreted before, by reference to our view that it would be an over-simplification to regard the transition from the bimolecular to the unimolecular mechanism of substitution as a sharp change. There must be degrees of coupling between the bond-breaking and bond-forming processes involved in a substitution, and, in conditions near to those which would change the mechanism, many molecules may react along paths which cannot clearly be classified as belonging to either mechanism. The consequence is that, as the conditions for a change of mechanism are approached, signs of the impending change, *e.g.*, particular types of variation of rate with structure or with solvent, may begin to appear before all the kinetic characteristics of the new mechanism are fully developed. One recognises that isolated small rate differences are unlikely in principle to have any simple relation to structure; and furthermore that some of the measurements of substitution rates involve a considerable experimental error. Nevertheless it is clear that the drop of rate with ascent of the homologous series is significantly less in the secondary alkyl series than in the primary alkyl series discussed in the preceding paper. It also seems fairly clear that the drop of rate with ascent of the secondary series is less with the weaker alkali than with the stronger. These tendencies accord with the ideas indicated, inasmuch as in passing from the primary to the secondary alkyl series, as well as in passing from more to less alkaline solutions, one is approaching more closely to the conditions in which the unimolecular mechanism takes control. It is possible to express the whole argument in terms of potential energy surfaces, as has been done in an analogous case (cf. Hughes, Ingold, and Shapiro, *loc. cit.*).

TABLE II.

Analysis of kinetic data for the reactions of secondary alkyl bromides with potassium hydroxide and with sodium ethoxide in ethyl alcohol, showing the variation of the rates of bimolecular substitution and bimolecular elimination with progressive changes in the structure of the alkyl group.

Conditions.	Series.	Alkyl bromide.	10^5k_2.	% Olefin.	10^5k (S_N2).	$10^5k(E2)$.	
						Total.	Each branch.
4N-KOH in EtOH at 80·0°	1	 $\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CHBr$	162	87·1	21	141	70 70
		 $\begin{array}{l}CH_3{\cdot}CH_2\\CH_3\end{array}\!\!>CHBr$	209	91·4	18	191	156 35
		 $\begin{array}{l}CH_3{\cdot}CH_2{\cdot}CH_2\\CH_3\end{array}\!\!>CHBr$	166	90·4	16	150	106 44
	2	 $\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CHBr$	162	87·1	21	141	70 70
		 $\begin{array}{l}CH_3{\cdot}CH_2\\CH_3\end{array}\!\!>CHBr$	209	91·4	18	191	156 35
		 $\begin{array}{l}CH_3{\cdot}CH_2\\CH_3{\cdot}CH_2\end{array}\!\!>CHBr$	211	96·8	7	204	102 102
1N-NaOEt in EtOH at 25·0°	1	 $\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CHBr$	0·295	80·3	0·058	0·237	0·118 0·118
		 $\begin{array}{l}CH_3{\cdot}CH_2\\CH_3\end{array}\!\!>CHBr$	0·422	82·2	0·075	0·347	0·282 0·065
		 $\begin{array}{l}CH_3{\cdot}CH_2{\cdot}CH_2\\CH_3\end{array}\!\!>CHBr$	0·343	80·7	0·067	0·276	0·196 0·080
	2	 $\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CHBr$	0·295	80·3	0·058	0·237	0·118 0·118
		 $\begin{array}{l}CH_3{\cdot}CH_2\\CH_3\end{array}\!\!>CHBr$	0·422	82·2	0·075	0·347	0·282 0·065
		 $\begin{array}{l}CH_3{\cdot}CH_2\\CH_3{\cdot}CH_2\end{array}\!\!>CHBr$	0·455	88·1	0·054	0·401	0·200 0·200

The simultaneous substitution and elimination reactions which the same series of secondary alkyl halides undergoes at 80·0° in neutral and acidic " 60% " aqueous ethyl alcohol have also been studied. The total reaction, as measured by the development of acidity, is now of the first order. In each case, we have measured the total rate constant, k_1, and also the proportion of olefin formed in the reaction. Since the olefin in these experiments is produced in acidic solutions the precautions, described in Part VI (this vol., p. 2041), had to be taken in order to obviate error due to loss of formed olefin through the acid-catalysed addition of solvent molecules to form an alcohol or an ether. The experimental results are in Table III. The value of the rate-constant for *iso*propyl bromide, as deduced from Hughes, Ingold, and Shapiro's results (*loc. cit.*) by extrapolation with respect to temperature, is $7{\cdot}83 \times 10^{-5}$ sec.$^{-1}$, and is thus higher than that now recorded. The most probable cause of the difference is a slight difference of solvent-composition. A still higher value, $9{\cdot}08 \times 10^{-5}$ sec.$^{-1}$, was recorded by Hughes and Shapiro (*J.*, **1937**, 1192); but in this case the solutions were deliberately made up in a complicated way for the purpose of a special comparison, and a difference of solvent-composition is to be expected. In the present experiments a single batch of " 60% " aqueous alcohol was drawn upon for all the rate determinations recorded in Table III.

The unimolecular substitution and elimination reactions, S_N1 and $E1$, have a common slow stage, *viz.*, the ionisation of the alkyl halide. If we knew that the whole of the observed first-

TABLE III.

First-order rate-constants (k_1 *in* sec.$^{-1}$), *and percentages of olefin formed, in the reactions of secondary alkyl bromides in neutral and acidic " 60% " aqueous ethyl alcohol at* 80·0°.

Alkyl bromides.	10^5k_1.		% Olefin.	
	Determinations.	Mean.	Determinations.	Mean.
2-Propyl	7·06, 7·06	7·06	4·7, 4·2, 4·9	4·6
2-*n*-Butyl	7·46, 7·37	7·41	8·7, 8·4	8·5
2-*n*-Amyl	5·61	5·61	5·8, 6·2, 5·7, 8·6	6·8
3-*n*-Amyl	5·91, 6·03	5·97	14·4, 14·3, 17·4, 14·3	15·1

order reaction were indeed unimolecular, then we should interpret the first-order rate-constant k_1, as measuring the rate of ionisation, and the proportion of olefin as giving the ratio in which the alkyl carbonium ion, produced by the ionisation, is partitioned in the final, rapid stages of substitution and elimination. However, it has been recognised since 1940 that some part of the first-order solvolytic reactions of secondary alphyl halides in aqueous alcoholic solvents consist of bimolecular substitutions in which a neutral solvent molecule is the substituting agent (Bateman, Cooper, Hughes, and Ingold, *J.*, 1940, 925; Dostrovsky, Hughes, and Ingold, *J.*, 1946, 191). The precise proportions in which these bimolecular solvolytic substitutions are present are still not exactly known, but attempts to secure definite measurements are in hand. From this situation it follows that neither the overall first-order constant, k_1, nor the proportion of olefin, can safely be concluded to have any simple and exact mechanistic significance. However, one may expect that, if the olefin proportions are used in order to analyse the total first-order rates into their constituent substitution and elimination rates, then any complications arising from the composite molecularity will become concentrated in the substitution constants, leaving the elimination constants with the significance of true unimolecular rate-constants. The reason for this expectation is that, when the basicity of a nucleophilic reagent is progressively reduced, its power of attacking hydrogen and thereby producing a bimolecular elimination disappears much more rapidly than its power of attacking carbon and thus participating in a bimolecular nucleophilic substitution (Hughes, Ingold, Masterman, and MacNulty, *loc. cit.*). Our knowledge of this phenomenon makes it appear most improbable that bimolecular eliminations involving solvent molecules as reagent could occur to any significant extent under the conditions of our measurements.

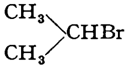
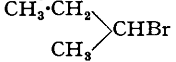
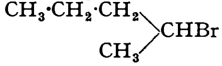
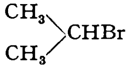
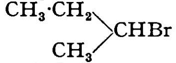
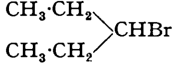
We have analysed the data of Table III on these lines, and the resulting figures are in Table IV. They are arranged to show the effects which arise from the progressive lengthening of a carbon chain, and from successively introduced β-linked methyl substituents. Our analysis is incomplete in the respect that although the olefins formed from 2-*n*-butyl and 2-*n*-amyl bromide will certainly be mixtures of isomerides, we have not analysed them owing to the difficulties created by the small yields. and have therefore been unable to split up the elimination constants, $k(E1)$, into components representing elimination along the different branches of the alkyl groups.

The substitution constants of Table IV show no marked and simple dependence on structure within the limits illustrated. This can be explained either on the grounds that the conditions are near those of mechanistic change, or by means of the theory that these constants represent rates of mixtures of substitution processes of different molecularities and largely opposing trends with respect to variation of rate with structure. On the other hand, the elimination constants have a simple and easily intelligible connexion with structure.

We shall here restrict comment on the elimination rates to pointing out the similarity in the structural variation of the bimolecular and the unimolecular elimination rates (cf. Tables II and IV). In the series *iso*propyl, *sec.*-butyl, 2-*n*-amyl, both the $E2$ and $E1$ rates increase fairly sharply from the first member to the second, and then decrease less sharply from the second to the third. In the series *iso*propyl, *sec.*-butyl, 3-*n*-amyl, both the $E2$ and $E1$ rates exhibit similar increases from the first to the second, and from the second to the third, of the homologues. The further analysis that was possible in the case of the bimolecular eliminations shows that every change of rate, no matter what its direction may be, from one compound to another is always more than accounted for by a change in the rate of establishment of the olefinic double bond in that branch of the alkyl group which has become altered, this effect being partly offset by opposite changes of smaller magnitude in the rate of entrance of the double bond into the

TABLE IV.

Analysis of kinetic data for the reactions of secondary alkyl bromides with " 60% " aqueous alcohol at 80·0°, *showing the variation in the first-order substitution rates and unimolecular elimination rates with progressive changes in the structure of the alkyl group.*

Series.	Alkyl bromide.	10^5k_1.	% Olefin.	10^5k (" S_N1 ").	$10^5k(E1)$.
1	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHBr$	7·06	4·6	6·74	0·32
	 $\left.\begin{matrix}CH_3\cdot CH_2\\CH_3\end{matrix}\right\rangle CHBr$	7·41	8·5	6·78	0·63
	 $\left.\begin{matrix}CH_3\cdot CH_2\cdot CH_2\\CH_3\end{matrix}\right\rangle CHBr$	5·61	6·8	5·23	0·38
2	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHBr$	7·06	4·6	6·74	0·32
	 $\left.\begin{matrix}CH_3\cdot CH_2\\CH_3\end{matrix}\right\rangle CHBr$	7·41	8·5	6·78	0·63
	 $\left.\begin{matrix}CH_3\cdot CH_2\\CH_3\cdot CH_2\end{matrix}\right\rangle CHBr$	5·97	15·1	5·07	0·90

alkyl branches which remain similar. The theoretical interpretation of these relationships will be considered in Part XVI.

EXPERIMENTAL.

Materials.—Commercial *iso*propyl bromide was dried and fractionated : it had b. p. 60°/760 mm. 2-*n*-Butyl, 2-*n*-amyl, and 3-*n*-amyl bromide were prepared by the action of hydrogen bromide on the pure synthetic alcohols. Dried and fractionated, they had b. p. 91·5°/757 mm., 118°/746 mm., and 117°/758 mm. respectively. The solvent ethyl alcohol was dried by Lund and Bjerrum's method. A large batch of " 60% " aqueous alcohol was made by mixing 3 vols. of anhydrous ethyl alcohol with 2 vols. of distilled water at 20°.

Methods for Kinetic Measurements.—Owing to the considerable concentrations of alkali present in the second-order reactions, these were followed by estimating halide ions by Volhard's method. Portions of the reaction mixture, usually 5 c.c., were enclosed in the cold in sealed tubes, which, after being heated in the thermostat, were broken each under 100 c.c. of 2·5N-nitric acid (halogen-free) and 60 c.c. of ether. The solution was shaken, and the aqueous layer, and a further aqueous extract of the ethereal layer, were run into 50 c.c. of ether and a known volume of standard silver nitrate solution. The excess of silver was then determined by titration with thiocyanate. In the experiments with sodium ethoxide, second-order rate-constants were calculated from the formula $k_2 = \{1/t(a - b)\}\log_e\{b(a - x)/a(b - x)\}$, where t is the time in seconds, a and b are the initial concentrations of sodium ethoxide and alkyl bromide, and x is the concentration of halide liberated at time t. In the experiments with concentrated potassium hydroxide, first-order constants were calculated from the formula $k_1 = (1/t)\log_e\{b/(b - x)\}$ where t, b, and x have their previous meanings; and then these constants were converted into second-order constants, k_2, by division by a, the initial concentration of the alkali. In both cases the second-order constants were corrected for the change of volume of the solvent between the temperature at which the solutions were made up and measured and the temperature of the thermostat.

The first-order reactions were also carried out in small sealed tubes, but in this case the development of acid was followed. Each tube containing a sample to be analysed was broken under 100 c.c. of acetone, and the liberated hydrogen bromide was titrated with standard alkali, with the use of lacmoid as indicator. First-order rate-constants were calculated from the formula $k_1 = (1/t)\log_e\{b(b - x)\}$, where the symbols have their previous meanings.

Method for Olefin Estimations.—The olefins were estimated by the extraction method, even propylene, although a correction of 6—8% for losses is necessary in this case (cf. Hughes, Ingold, Masterman, and MacNulty, *loc. cit.*). The estimations of olefin formed in the alkaline solutions were made as described in the preceding paper : the amounts of halide ion and olefin simultaneously present at two times, one near the beginning and one towards the conclusion of a run, were estimated, and the proportion in which the reaction results in olefin was calculated from the differences. The estimations of olefin formed in acid solution required a " pilot " experiment, in which olefin and halide ion were estimated at various times during the course of a run in order to discover the range of times during which the most accurate estimates could be made. Such times were used in subsequent estimations. The best times are those which allow as long as possible for the development of olefin, before the disappearance of olefin, through acid-catalysed solvent-addition, becomes appreciable. The corrections for losses of olefin, which are hardly appreciable except in the case of propylene, were determined by blank experiments.

Results of Measurements.—These are summarised in Tables I and III. Examples of the different types of measurement are given in Tables V—X.

TABLE V.

Illustrating determinations of first- and second-order rate-constants (k_2 *in* $sec.^{-1}$ *g.-mol.*$^{-1}$ *l.*; k_1 *in* $sec.^{-1}$) *in reactions of secondary alkyl bromides with* 4N-*ethyl-alcoholic potassium hydroxide* : iso*propyl bromide.*

(Solvent: EtOH. Temp. 80·0°. Initially [$\mathrm{Pr^iBr}$] = 0·1503M and [KOH] = 3·955N. In this Table [$\mathrm{Pr^iBr}$] is expressed in c.c. of 0·07333N-thiocyanate per 5 c.c. sample.)

t (min.).	[$\mathrm{Pr^iBr}$].	10^4k_1.	10^4k_2.
0·0	10·25	—	—
0·5	8·55	60·4	15·2
1·0	7·01	63·3	16·0
1·5	5·80	63·2	16·0
2·0	5·10	58·1	14·7
2·5	4·20	59·5	15·0
3·5	2·92	59·8	15·1
4·5	1·95	61·4	15·5
5·5	1·40	60·3	15·2
6·5	0·95	60·9	15·4
7·5	0·70	59·6	15·0
8·5	0·50	59·2	14·9
10·0	0·30	58·8	14·8
15·0	0·10	—	—

(Mean 10^4k_1 = 60·3. Mean 10^4k_2 = 15·3. Corrected for expansion 10^4k_2 = 16·2.)

TABLE VI.

Illustrating determinations of olefin proportions in reactions of secondary alkyl bromides with 4N-*ethyl-alcoholic potassium hydroxide* : iso*propyl bromide* (*Expt. A*).

(Solvent: EtOH. Temp. 80·0°. Initially [$\mathrm{Pr^iBr}$] = 0·1582M and [KOH] = 3·955N. Portions of 10 c.c. used for estimation of bromide ion and olefin. In the Table the bromide ion is given by the silver, measured in c.c. of 0·09065N-thiocyanate, which survives out of 20 c.c. of added standard silver nitrate, and the olefin is given by the bromine, measured in c.c. of 0·1686N-thiosulphate, which remains out of 10 c.c. of added standard bromine.)

Initial readings.		Final readings.	
Silver.	Bromine.	Silver.	Bromine.
22·75	36·6, 36·3, 36·8, 36·4	5·20, 5·25	21·4, 21·0, 21·2, 21·8
22·70	36·7, 36·5, 36·6	5·31	21·6, 21·6, 20·8
22·73 (mean)	36·55 (mean)	5·27 (mean)	21·20 (mean)

(Proportion of olefin = 81·8%. Proportion corrected for losses = 88·0%.)

TABLE VII.

Illustrating determinations of second-order rate-constants (k_2 *in* $sec.^{-1}$ *g.-mol.*$^{-1}$ *l.*) *in reactions of secondary alkyl bromides with* 1N-*alcoholic sodium ethoxide* : iso*propyl bromide.*

(Solvent: EtOH. Temp. 25·0°. Initially [$\mathrm{Pr^iBr}$] = 0·2054M and [NaOEt] = 0·9783N. In the Table [$\mathrm{Pr^iBr}$] and [NaOEt] are both expressed in c.c. of 0·09049N-thiocyanate per 5 c.c. sample.)

t (min.).	[NaOEt].	[$\mathrm{Pr^iBr}$].	10^6k_2.
0	54·06	11·35	—
115	53·84	11·13	2·90
195	53·68	10·97	2·95
395	53·31	10·60	2·96
740	52·76	10·05	2·83
1355	51·76	9·05	2·91
1895	51·01	8·30	2·90
2735	50·11	7·40	2·77
3515	49·11	6·40	2·92
4235	48·31	5·60	3·02
4955	47·81	5·10	2·94
5720	47·26	4·55	2·93
7200	46·41	3·70	2·90
8640	45·71	3·00	2·90
9025	45·51	2·80	2·93
10045	45·14	2·43	2·92
11465	44·86	2·15	2·78
22305	43·21	0·50	2·80
24785	43·09	0·38	2·76
" ∞ "	42·71	0·00	—

(Mean 10^6k_2 = 2·88. Corrected for expansion of solvent, 10^6k_2 = 2·95.)

TABLE VIII.

Illustrating determinations of olefin proportions in reactions of secondary alkyl bromides with 1N-*alcoholic sodium ethoxide* : iso*propyl bromide* (*Expt. A*).

(Solvent: EtOH. Temp. 25·0°. Initially [$\mathrm{Pr^iBr}$] = 0·1815M and [NaOEt] = 0·9784N. Portions of 10 c.c. used for the estimation of bromide ion and olefin. In the Table the bromide ion is given by the silver, measured in c.c. of 0·0899N-thiocyanate, which survives out of 20 c.c. of added silver nitrate, and the olefin is given by the bromine, measured in c.c. of 0·2556N-thiosulphate, which remains out of 10 c.c. of added standard bromine.)

Initial readings.		Final readings.	
Silver.	Bromine.	Silver.	Bromine.
26·10	25·12, 24·85, 24·80	5·92	13·25, 14·18, 13·65
26·10	24·40, 24·45, 24·60	5·90	14·13, 13·85, 13·45
26·10 (mean)	24·70 (mean)	5·91 (mean)	13·75 (mean)

(Proportion of olefin = 77·1%. Proportion corrected for losses, 82·7%.)

TABLE IX.

Illustrating determinations of first-order rate-constants (k_1 *in sec.*$^{-1}$) *in reactions of secondary alkyl bromides in initially neutral aqueous ethyl alcohol :* iso*propyl bromide* (*Expt. A*).

(Solvent : " 60% " aqueous EtOH. Temp. 80·0°. Initially [$\mathrm{Pr^iBr}$] = 0·1341M. In the Table [$\mathrm{Pr^iBr}$] is expressed in c.c. of 0·0514N-alkali per 5 c.c. sample.)

t (min.).	[$\mathrm{Pr^iBr}$].	10^5k_1.	t (min.).	[$\mathrm{Pr^iBr}$].	10^5k_1.
0	13·05	—	184	6·00	7·03
10	12·50	7·14	219	5·20	7·00
20	12·00	6·96	254	4·48	7·01
30	11·48	7·11	314	3·40	7·14
45	10·80	7·00	374	2·70	7·02
59	10·10	7·23	464	1·85	7·01
79	9·24	7·28	554	1·20	7·17
104	8·48	6·90	634	0·85	7·18
144	7·15	6·96	1352	0·40	—

(Mean 10^5k_1 = 7·06.)

TABLE X.

Illustrating determinations of olefin proportions in reactions of secondary alkyl bromides in initially neutral aqueous ethyl alcohol : iso*propyl bromide* (" *Pilot* " *Expt. A*).

(Solvent : " 60% " aqueous EtOH. Temp. 80·0°. Initially [$\mathrm{Pr^iBr}$] = 0·1482M. Portions of 10 c.c. taken for estimation of acid and olefin. In the Table the acid is expressed in c.c. of 0·07142N-alkali, and the olefin is given by the bromine, measured in c.c. of 0·1176N-thiosulphate, which survives out of 5 c.c. of added standard bromine.)

	Acid.		Bromine.		Olefin, %.	
t (min.).	Readings.	Mean.	Readings.	Mean.	Uncorr.	Corr.
0	0·50 0·50	0·50	25·75, 25·35 25·85, 25·45	25·60	—	—
92	7·18 7·22	7·20	25·20, 25·50 24·90, 25·55	25·28	3·90	4·20
142	9·80 9·90	9·85	24·95, 25·18 24·80, 25·31	25·06	4·75	5·12
214	12·95 12·85	12·90	25·50, 25·68 25·48, 25·27	25·48	0·80	0·87
390	17·10 17·02	17·06	25·90, 25·35 25·60, 25·40	25·56	0·19	0·20
1080	21·25 21·25	21·25	25·80, 25·70 25·40, 25·60	25·62	—	—

(In consequence of these results, the readings in the main series of experiments were taken initially and after times in the range 90—150 mins. In these experiments portions of 30 c.c. were taken for the olefin estimation in order to increase the accuracy.)

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