50. *Mechanism of Substitution at a Saturated Carbon Atom. Part VI. Hydrolysis of* iso*Propyl Bromide.*

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A recent publication (Taylor, J., 1935, 1514) opens with the following passage : " Hughes and Ingold (this vol., p. 246) have discussed the two types of mechanism—S_N1 and S_N2—for substitution by the nucleophilic hydroxyl ion at a saturated carbon atom. An entirely distinct mechanism is now brought forward to explain olefin formation when hydroxyl ion reacts with bromo- (and other halogeno-) ethanes." A detailed description of the mechanism follows this statement. As this mechanism (it is our E2) for the formation of olefins in hydrolysis was advanced by Hanhart and Ingold in 1927, and has since been discussed by Hughes or Ingold in eleven papers on 'onium ions, three on sulphones, and three on halogeno-paraffins, by von Braun in three papers on 'onium ions, and by Olivier in two papers on halogeno-paraffins, not to mention many references by other authors and a brief résumé in the *Annual Reports* for 1930, it would appear that the statement quoted obscures the history of the matter. Even Taylor's specific application of the mechanism (to the alternative olefin eliminations of polyhalogeno-compounds) was made, correctly and with adequate detail, by Olivier in 1934. Our general mechanisms are formulated for later reference; the numerical parts of the labels are reminders of the kinetic types to which the mechanisms belong :

$$\overset{\curvearrowright}{\mathrm{Y}}\ \ \mathrm{Alk}\overset{\curvearrowright}{—}\mathrm{X} \longrightarrow \mathrm{Y}—\mathrm{Alk} + \mathrm{X} \quad .\ .\ .\ .\ .\ . \quad (S_N2)$$

$$\left.\begin{array}{r} \mathrm{Alk}—\mathrm{X} \longrightarrow \mathrm{Alk}^+ + \mathrm{X}\ (\text{slow}) \\ \overset{\curvearrowright}{\mathrm{Y}}\ \ \mathrm{Alk}^+ \longrightarrow \mathrm{Y}—\mathrm{Alk}\ (\text{fast}) \end{array}\right\} \quad .\ .\ .\ .\ . \quad (S_N1)$$

$$\overset{\curvearrowright}{\mathrm{Y}}\ \ \mathrm{H}\overset{\curvearrowright}{—\mathrm{C}—}\mathrm{C}\overset{\curvearrowright}{—}\mathrm{X} \longrightarrow \mathrm{YH} + \mathrm{C}{=}\mathrm{C} + \mathrm{X} \quad .\ .\ .\ . \quad (E2)$$

We record below a kinetic study of the hydrolysis of *iso*propyl bromide, a key example as will appear, since the two substitutions S_N2 and S_N1 and the elimination E2 are all present together, and can be shown to exhibit recognisably distinct kinetic characteristics. We here explain briefly the relation of this research to its predecessors.

In Part I (J., 1933, 526), Hughes, Ingold, and Patel discussed theoretically the nucleophilic substitution mechanisms S_N2 and S_N1 *inter alia.* They predicted (although there was then no kinetic evidence on the matter) that in a series Alk·X, such as

$$\mathrm{MeX, EtX, Pr^{\beta}X, Bu^{\gamma}X} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (I)$$

in which Alk steadily increases in its power of electron release, S_N2 should prevail up to a certain point, after which S_N1 should take control; and that accordingly, before the transition point the substitution should exhibit second-order kinetics and an absolute rate decreasing with progression through the series, whilst after it, the kinetics should be first-order and the rate an increasing one. These and a number of other analogous predictions were verified in all detail when, in Part III (J., 1935, 236), Gleave, Hughes, and Ingold recorded the completion of a kinetic study of nucleophilic substitutions in structures of the form $\mathrm{Alk{\cdot}\overset{+}{S}R_2}$. For the reaction with hydroxide ions in water, for example, the mechanistic transition point in the above series was located between the ethyl and the *iso*propyl compounds. The next case to be considered was the analogous reaction of alkyl halides, to which, of course, the same predictions apply. In this field it was already known from the work of de Bruyn and Steger (*Rec. trav. chim.*, 1899, **18**, 41, 311) and Grant and Hinshelwood (J., 1933, 258) that methyl and ethyl halides undergo bimolecular reactions with alkali in alcohol or aqueous alcohol. Then Hughes showed in Part V (J., 1935, 255) that the hydrolysis of *tert.*-butyl chloride in aqueous alcohol or aqueous acetone is a reaction of the first order. This proved the presence of a mechanistic transition point somewhere in the alkyl series, but its location required the study of *iso*propyl halides.

With regard to the olefin elimination, E2, the most interesting question is whether it can be shown to be kinetically independent of the simultaneous substitution, as of course it must be if the mechanistic theories formulated above are correct. In the sulphonium ion series (I; $X = \overset{+}{S}R_2$), olefin elimination accompanies the hydrolysis of the ethyl, *iso*propyl, and *tert.*-butyl compounds. In the last case the substitution and elimination are obviously independent, since one is a reaction of the first order and the other one of the second. In the ethyl derivative, however, both the substitution and the elimination are second-order reactions. Possibly an experimental distinction could be drawn on the basis of the temperature coefficients of the rate constants, but this has not yet been done. In the alkyl halide series (I; X = Hal.), an appreciable olefin reaction accompanies hydrolytic substitution only in the cases of ethyl and *iso*propyl halides; and of these, only the ethyl compounds have previously been made the subject of kinetic measurements. Brussoff (*Z. physikal. Chem.*, 1900, **34**, 129) proved the occurrence of both reactions, and Grant and Hinshelwood (*loc. cit.*) measured the rate of the two together, but not of either separately. These authors considered the question of the possible kinetic independence of the two reactions, and showed that if they were independent this did not upset the fitting of the total rate constant to Arrhenius's equation. However, this is a hard test for independence, because unless both reactions are present in rather similar proportions (which according to both Brussoff and Grant and Hinshelwood is not the case), and unless also their (Arrhenius) energies of activation are well separated, the total rate constant would be likely to fit the equation anyhow.

As mentioned above, we have proved that the bimolecular and unimolecular substitutions and the bimolecular elimination are all present together in the hydrolysis of *iso*propyl bromide in aqueous alcohol. Further, we have measured the separate rate constants of the three reactions, studied the effect of solvent changes on each, and measured their separate temperature coefficients.*

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* The circumstance that we can analyse the total substitution into components of different order is quite consistent with the view that no sharp line of demarcation exists between the two mechanisms, or, as Gleave, Hughes, and Ingold expressed it, that there are " *degrees* of collaboration " by the reagent in the work of removing the replaceable group (*loc. cit.*, p. 238).

The method is as follows. A first-order reaction is isolated by the use of low concentrations of hydroxide ions, *i.e.*, by the employment of acidic or quite dilute alkaline solutions (cf. Hughes, *J. Amer. Chem. Soc.*, **1935**, **57**, 708). No propylene is formed under these conditions, so that the reaction, measured by loss of alkalinity, increase of acidity, or liberation of bromide ions, must be the unimolecular substitution (S_N1) leading to *iso*propyl alcohol. At somewhat larger initial concentrations of hydroxide ions (*e.g.*, 0·1*N*) a " constant " calculated from the first-order formula falls during a run, and the fall becomes more marked the greater the initial alkalinity. This is due to the incursion of a second-order reaction. Correspondingly, the " constant " calculated from the second-order formula rises during a run, and the rise becomes less marked with each increase of the initial alkalinity. The previous determination of the true first-order constant enables us to calculate a true second-order constant. Concurrently with the incursion of the second-order process, propylene begins to appear amongst the products. A method has been developed by means of which the propylene can be accurately estimated by means of its reaction with bromine. It is found that the production of propylene accounts for only about half of the total second-order reaction, and is itself a second-order reaction (E2). The balance of the total second-order reaction represents the bimolecular substitution (S_N2) leading to *iso*propyl alcohol.*

Concerning the substitution process in the hydrolysis of alkyl halides, it will be apparent that the point at which the mechanism changes in the series Me, Et, Pr^{β}, Bu^{γ} has been located *at* the *iso*propyl group, for our solvents and concentrations. The comparison of absolute rates is not quite straightforward, but may be made as follows. De Bruyn and Steger (*loc. cit.*) studied the hydrolysis of methyl and ethyl iodides in a range of mixtures of ethyl alcohol and water, and it is clear from their results that the ethyl compound reacts more slowly. This is true even although the rate constants for ethyl iodide include the rate of olefin formation : for 80% ethyl alcohol as solvent, the ratio of the rates was 10 : 1, and this must be regarded as a conservative estimate of the ratio of the rates of the pure substitution processes. Grant and Hinshelwood (*loc. cit.*) measured the rate of hydrolysis of ethyl bromide in 100% ethyl alcohol, and we have studied the hydrolysis of *iso*propyl bromide in 60% and 80% ethyl alcohol but not in pure alcohol. As the measurements stand, the *iso*propyl halide reacts the more slowly, the ratio of Grant and Hinshelwood's rate in pure alcohol to our second-order rate (for the substitution alone) in 80% alcohol being 46 : 1. This ratio needs correction, however, first because the rate for ethyl bromide includes the rate of olefin formation, and secondly because the solvents differ. (In the latter connexion we have to consider, not only the environmental influence of the solvent, but also the circumstance that the reaction leading to an ether could not have been a negligible constituent of Grant and Hinshelwood's measured rate.) The first correction will reduce the ratio, but not by much, since Grant and Hinshelwood state that the proportion of olefin formed is small. The second correction will also reduce the ratio, but again by a rather small factor, the order of magnitude of which can be estimated from various results, *viz.*, de Bruyn's, Hinshelwood's, Taylor's, and our own. Taking everything into account, it would appear that the real ratio must lie in the neighbourhood of 25 : 1. Thus there is continuous diminution in the series, Me, Et, Pr^{β}, with regard

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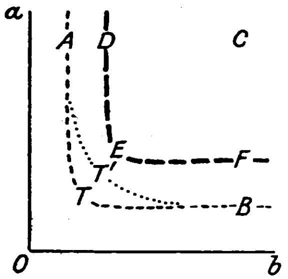
* Two solvents were employed, *viz.*, 60% and 80% aqueous ethyl alcohol. In the latter solvent, 20—30% of the product of the unimolecular substitution (S_N1) is actually ethyl *iso*propyl ether. However, the alcohol in the solvent intervenes only in the fast stage of this reaction, and the only concentration entering explicitly into the velocity equation is that of *iso*propyl bromide. In the same 80% alcoholic solvent, about 2% of the total bimolecular reaction (S_N2 + E2) results in the formation of the ether, and this means that about 5% of the bimolecular substitution (S_N2) represents replacement of the halogen by OEt, and 95% replacement by OH. Here the measured rate involves the concentration of the attacking anion, which in the text is taken as OH^-, the fact that a little of it is really OEt^- being disregarded for the sake of simplicity. This is justified because the effect of the minor reaction on the determinations of critical energy would be inappreciable, provided that, as is extremely probable, the critical energies of the reactions of the two anions do not differ by more than 2 or 3 kg.-cals. For the other solvent, 60% alcohol, the proportions in which ether is formed are smaller, and, in the case of the bimolecular reaction, barely appreciable.

to the second-order rates. The first-order rate constants for *iso*propyl bromide (this paper) and *tert.*-butyl chloride (Hughes, *loc. cit.*) in 80% alcohol at 45° stand in the ratio 1 : 134, and it is known qualitatively that *tert.*-butyl bromide is hydrolysed considerably more rapidly than the chloride. Thus there is a very marked increase from Pr^{β} to Bu^{γ}, with respect to first-order rates. These are just the predicted effects.

When previously discussing such relations, Hughes and Ingold foresaw the possibility that in some series, ascending in the electron release of the alkyl substituent, the change from a decreasing to an increasing rate might occur at an earlier point than the change from second- to first-order kinetics; but they could not find a clear example. Since then, Baker and Nathan have produced one in their study of the reaction between substituted benzyl bromides and pyridine (J., 1935, 1840). Accordingly, we may set forth this feature in the theory more fully than heretofore. We know that in a bimolecular reaction the associative and dissociative processes cannot be given separate energies, and yet it has to be shown why we might expect a progressively increasing electron accession to the reaction zone to act in the early stages as though it was principally occupied in repelling the reagent, and (perhaps) at a later stage as though it were mainly engaged in expelling the replaceable group (even though the reaction is still bimolecular). The situation is most easily understood with the aid of an imaginary potential surface (see fig.), which we assume to possess not only the two valleys *A* and *B* usual for a gas reaction with a transition state at *T*, but also a third valley at *C* (due to ion solvation) together with the included pair of ridges *DEF*. With increasing electron accession to the reaction zone we expect an increasing gradient, negative in directions *Oa* and *Ob*, to be imposed on the original surface. The first effect of this will be to raise the energy of the activation *AT*, the reaction track *ATB* undergoing originally only a very slight displacement away from the origin. At a later stage, however, when the increasing tilt has depressed the ridges *DEF* and largely flattened the hill *TE*, the reaction track *AT′B* will fan out much more widely. This would lead to a reduced increase, and possibly an actual decrease, in the activation energy, and in certain cases the decrease might set in before the reaction track has become so far turned that the representative point runs over into valley *C* (unimolecular reaction). This explains why comparable structural changes always affect the rate of a bimolecular substitution less strongly than that of the allied unimolecular reaction (examples reported or quoted in these papers) : the former effect is a difference, even although the separate terms cannot be associated each exclusively with the formation or rupture of a bond.



In advancing this interpretation, we are not perturbed by the fact that in Baker and Nathan's series, as well as in a number of others where no rate minimum has been found, the rather small changes of rate with structure are found to be correlated more with changes of *P* than with changes of *E* when the equation $k = PZe^{-E/RT}$ is applied. Baker and Nathan's series belongs to the important group of those which avoid local effects due to substitution very close to the site of reaction; and within this group it is the rule that large changes of absolute rate are correlated essentially with changes of *E*—exactly as the electronic theory of reaction mechanism requires that the changes of rate should be correlated with changes of the critical energy (preceding paper). Now a critical energy which theory treats as a structural constant is evidently not to be identified *exactly* with the Arrhenius critical energy, *E*, which, like *P*, is a function of temperature. An apparent straightness in the usual logarithmic plot over perhaps a 10—15% range of *T* does not furnish a good reason for disregarding this distinction, since an inappreciable difference of slope between two halves of such a plot could easily correspond to a considerable difference between the mean slope and its limit $T \longrightarrow 0$.* This does not mean that it is useless to examine the dependence of changes of rate with structure and solvent on changes in the

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* A new experimental demonstration of the temperature dependence of the Arrhenius critical energy has been published by La Mer and Miller (*J. Amer. Chem. Soc.*, 1935, **57**, 2674).

Arrhenius parameters; but it does mean that the results should be interpreted with reserve unless the differences are large.

To avoid misconception it may be added that we recognise the existence of structural series in which large changes of the rate are correlated largely with changes of P; however, the circumstances in which this can happen seem to be fairly clear. Structural series may be divided into two chief classes according to whether local effects are absent or present. If they are absent, a further sub-division is possible according to whether or not the effect of the distant substituent can be carried by an electrically conducting (unsaturated) system the whole of the way to the site of reaction. If it can, then the changes of rate may be large, and if so they will be correlated essentially with changes of E (examples: aroylation of arylamines; hydrolysis of benzoic esters, see preceding paper). However, as we have seen, there are bimolecular reactions sufficiently near to the border region between bimolecular and unimolecular mechanisms to exhibit a marked reduction or even an inversion of the normal critical energy differences, so that a simple relation between rate and the Arrhenius energy E is not always to be expected. If an electrically conducting system does not extend from the distant substituent to the reaction zone, then in any case the changes of rate will be relatively small and their relation to E more or less obscured (*e.g.*, halogen exchange in β-arylthioethyl chlorides; Baddeley and Bennett, J., 1933, 261). The remaining alternative is that local effects are present. In this case the general result is that both P and E are changed, possibly quite largely, P because local substitution must seriously affect the entropy of the transition state (cf. Evans and Polanyi, *Trans. Faraday Soc.*, 1934, **31**, 875), and E because, even in a non-conducting (saturated) system, the variable group will in general be near enough to the reaction zone to affect the energy of the transition complex through dipolar, dispersion, or steric repulsive forces (*e.g.*, esterification, quaternary ammonium salt formation; Hinshelwood, Winkler and Legard, J., 1934, 1079; 1935, 587, 1147, 1588). These forces are mentioned in order of decreasing range, and it can readily be understood how, in particular cases, a substituent situated just beyond the distance from which it can largely influence the energy of activation may yet affect its entropy considerably.

The temperature coefficients of the three simultaneous reactions occurring in the hydrolysis of *iso*propyl bromide are distinct though not at all widely different. In " 60% " aqueous alcohol E for the unimolecular substitution is 22,690 cals. For the bimolecular substitution it is 20,760 cals., and for the bimolecular elimination 22,100 cals. In spite of the difference of 1340 cals. between their energies, the two bimolecular rates when added together give a sum which fits the Arrhenius equation very well.

Comparison of the results obtained with " 60% " and " 80% " ethyl alcohol as solvent shows that the addition of water to the alcoholic medium rather strongly accelerates the unimolecular reaction, slightly retards the bimolecular substitution, and somewhat more strongly retards the elimination. All these effects agree with, and could have been predicted from, Hughes and Ingold's theory of solvent action (J., 1935, 252). An analysis in terms of the factors of the Arrhenius equation is given but the differences are rather small and quite irregular. In a discussion which disregards the uncertainties attaching to the interpretation of the Arrhenius parameters, Taylor (*loc. cit.*) has complained that the solvent theory neglects the non-exponential rate factor. Actually, of course, this factor is recognised, but an analysis involving its separate treatment is precluded by the absence at the present time of a tractable theoretical method, even for reactions in the gaseous phase (cf. J., 1935, 246). It may be noted that, since both the temperature coefficient and the retarding effect of water are greater for the olefin reaction than for substitution, and since a high concentration suppresses the unimolecular substitution, the best yields of olefin will be obtained by avoiding water and using a high concentration and temperature—just the conditions which, to judge from preparative recipes (" hot strong alcoholic potash "), have long since been considered the most appropriate for the production of olefins generally. The rate constants are summarised in Tables X and XI.

EXPERIMENTAL.

Materials.—The *iso*propyl bromide was dried with anhydrous sodium carbonate and calcium chloride and fractionated, the fraction, b. p. 60°/760 mm., being used for the measurements. Commercial absolute alcohol was dried over lime and fractionated. The "60%" aqueous alcohol was made by mixing 6 l. of this absolute alcohol with 4 l. of water, and the "80%" aqueous alcohol by mixing 8 l. of the alcohol with 2 l. of water.

Rate Measurements.—The thermostats could be set to within 0·05°. The usual initial concentration of *iso*propyl bromide was $N/10$. The reaction mixture was enclosed in the cold in portions of 5 c.c. in sealed tubes, which were placed in the thermostat for known times, and then broken under 100 c.c. of absolute alcohol. Two methods of estimation were used. In the first the acid or alkali was titrated with, *e.g.*, $0{\cdot}02N$-sodium hydroxide (carbonate-free) or hydrochloric acid, lacmoid being used as indicator (phenolphthalein is inapplicable in the presence of much alcohol). In the second method, bromide ion was estimated in the neutralised or faintly acidic solution by titration with, *e.g.*, $0{\cdot}01N$-silver nitrate in the presence of eosin (adsorption indicator). For acidic or dilute alkaline solutions ($< 0{\cdot}1N$-alkali) either method may be used, and usually both were employed with concordant results, the second being applied to the solution obtained after completion of the first. For more strongly alkaline solutions the first method is less accurate, and the estimations were made by the second method.

Estimation of Propylene.—The sealed tube enclosing 5 c.c. of the reaction mixture containing the propylene to be estimated was broken by shaking under water, containing enough sulphuric acid to neutralise the alkali, in an evacuated stoppered jar provided with an inlet and an outlet tube, the former reaching to the bottom. By means of a slow stream of nitrogen, the propylene was swept through a trap at − 5° and through two bubbling tubes containing known quantities of a standard solution of bromine in chloroform. The second tube was kept at 0°, and a trap containing aqueous potassium iodide was placed at the end of the gas train. The jar being kept at 50—60°, the whole of the propylene could be swept over in ¾ hour and estimated by titrating the remaining bromine with standard thiosulphate.

The First-order Reaction.—A reaction was started in dilute alkaline solution ($N/200$) in "60%" alcohol and followed by titration with standard acid until the original alkali had disappeared. A good first-order constant was obtained. The experiment was then continued, and the development of free acid followed by titration with standard alkali. A good first-order constant was again obtained. The two first-order constants agreed to within 1% (Table I). For further kinetic investigation of the first-order reactions, initially neutral solutions were used for convenience. The rate was measured in the two solvents "60%" and "80%" aqueous alcohol, and at four temperatures (Tables II and III). It was shown that increasing the concentration of *iso*propyl bromide from the usual $M/10$ to $M/5$, and adding sodium bromide ($M/7$) initially, had only very small effects on the rate. Some of these experiments were done by the method of pipetting the samples and others by the sealed-tube method; but since in each case the initial concentration of *iso*propyl bromide was estimated for the calculation of the constants by an analysis made in the same way after completion of the reaction, it follows that the constants are unaffected by the deviations of concentration arising from the rather considerable thermal expansion of alcohol. It was proved that no propylene is formed under the conditions of the experiments.

The Total Second-order Reaction.—In $N/50$-alkaline solution the first-order constant shows a just perceptible drift throughout the reaction. The drift, a descent with increasing time, becomes more marked in stronger solutions until, in $N/5$-alkali, the first-order formula is quite inapplicable. On the other hand, the second-order formula is inapplicable in $N/50$-alkali, the "constant" rising rapidly during a run; but in more concentrated alkali the rise becomes less marked until in N-alkali it has become inappreciable. These observations led to the assumption that first- and second-order reactions are present together (Table IV). Assuming that the presence of the sodium hydroxide does not cause any marked change in the first-order velocity, the determined value for this may be used to calculate the second-order constant by a method described later. This was done for the "60%" alcoholic solvent and initial concentrations of sodium hydroxide ranging from $N/10$ to N, and it was found that the second-order constant fell by about 40% over this range (Table VII). It is believed that this effect is due to the ionic strengths of the solutions, since the application in the calculations of the activity coefficients of sodium hydroxide in water (the activities in 60% ethyl alcohol being unknown) brings the constants much closer together. The main series of determinations of the second-order constant were carried out in N-alkaline solution in order that the measurement should be as direct as possible; at this concentration over 90% of the whole reaction is of the second order. Measurements were made in " 60% " and in " 80% " alcohol, in the former solvent at three temperatures and in the latter at two (Tables V and VI). These determinations were all made by the method of separate sealed tubes and are therefore subject to an error due to thermal expansion of the solvent: the concentrations used in the evaluation of the reaction rate are based on a measurement of volume made at room temperature and are therefore greater than the actual concentrations obtaining during reaction at higher temperatures. Since second-order rate constants involve the reciprocal of a concentration it follows that they must be affected, even though the initial concentrations of reactants were determined from an analysis made after the completion of reaction. The error, which is probably just outside the limits of consistency of the observations, is not appreciably greater in " 80% " aqueous alcohol than in " 60%."

The Olefin Elimination.—From the determined values of the first- and second-order rate constants it is possible to calculate what proportion of the total reaction which has occurred at any time (or at infinite time) is of the second order. It is also possible to estimate the amount of olefin formed by the method described above. It was found that this only accounts for a part of the total second-order reaction. The olefin reaction was shown to be of the second order by the demonstration (*a*) that the amount of olefin formed at various times during a run is a constant fraction of the total second-order reaction taking place in the same times, and (*b*) that the amount of olefin formed on completion of different runs with different initial concentrations of alkali is a constant fraction of the total second-order reaction occurring in these runs. Both ratios were constant to within 1% (Table VIII). Having demonstrated this, it was necessary only to measure the olefin formed on completion of any run with a solvent and temperature for which the first- and second-order rate constants were known in order to find the ratio in which the second-order rate constant should be split up between the second-order substitution and the elimination. This was done for " 60% " alcohol at four, and for " 80% " alcohol at three temperatures (Table IX).

Calculation of the Total Second-order Rate Constant.—The problem is to calculate the second-order constant, given the first, from observations of the total reaction. The formula used, which is very convenient, is easily derived for the general case of two reactions, of order m and n, which may be either simultaneous or opposing. In either case let the reaction rate be governed by the equation

$$dx/dt = k_m f_m(x) + k_n f_n(x)$$

where f_m and f_n are the appropriate functions of concentration. Define a quantity $\mathbf{k}_n$ by the relation

$$\mathbf{k}_n = \frac{1}{t}\int_0^x \frac{dx}{f_n(x)} = \frac{1}{t} \cdot J$$

where J is simply an abbreviation for the definite integral. This amounts to applying to the whole reaction the integrated velocity equation of its nth order constituent; the " constant " thus obtained is not the true constant k_n, or even a constant at all, but is a function of x and therefore of t. By plotting it against t we can find the value, for any t, of the expression $t(d\mathbf{k}_n/dt)$. Then we have

$$\mathbf{k}_n + t\frac{d\mathbf{k}_n}{dt} = \frac{dJ}{dt} = \frac{dJ}{dx} \cdot \frac{dx}{dt} = \frac{1}{f_n(x)} \cdot \frac{dx}{dt} = k_m \frac{f_m(x)}{f_n(x)} + k_n$$

If k_m is known, k_n can be obtained at once, and if k_m is not known both k_m and k_n can be calculated by cyclic approximation, using the same formula with repeatedly interchanged subscripts. In our case we define $\mathbf{k}_2$ by the equation

$$\mathbf{k}_2 = \frac{1}{t(b-a)} \cdot \log_e \frac{b(a-x)}{a(b-x)} \quad \left[\text{or } \mathbf{k}_2 = \frac{1}{ta} \cdot \frac{x}{a-x} \text{ in case } a = b\right]$$

and calculate k_2 from

$$k_2 = \mathbf{k}_2 - \frac{k_1}{b-x} + t \cdot \frac{d\mathbf{k}_2}{dt}$$

The equation is exact, but the three terms on the right-hand side are of successively decreasing importance so long as most of the reaction is of the second order, and indeed in these circumstances the last term is often negligible.

Calculation of Separate Second-order Rate Constants.—In order to be able to split up k_2 into its two constituents, it is necessary to calculate the proportion $x_1/(x_1 + x_2)$ in which a reaction $x = x_1 + x_2$ has proceeded through the unimolecular route. For this purpose we decompose the equation

$$dx/dt = k_1(a - x) + k_2(a - x)(b - x)$$

into its two constituents,

$$dx_1/dt = k_1(a - x_1 - x_2)$$
$$dx_2/dt = k_2(a - x_1 - x_2)(b - x_1 - x_2),$$

divide the second by the first

$$dx_2/dx_1 = (k_2/k_1)(b - x_1 - x_2)$$

and integrate, using the condition $x_2 = 0$ when $x_1 = 0$ in order to evaluate the constant of integration. The result is

$$x_1 = (k_1/k_2) \log_e[\{(k_1/k_2) + b\}/\{(k_1/k_2) + b - x\}],$$

and the approximation

$$x_1/(x_1 + x_2) = x_1/x = k_1/\{k_1 + k_2(b - \tfrac{1}{2}x)\}$$

may be used when x is small.

Results for the First-order Rate Constants.—Tables I, II, and III relate to first-order rate constants (reaction S_N1) calculated from the formula $k_1 = (1/t) \log_e\{a/(a - x)\}$, where a is the initial concentration of *iso*propyl bromide and x the decrease of concentration; a was determined by measuring the asymptotic value of x at large times. Table I illustrates an experiment showing that the first-order rate constant is the same in a dilute alkaline as in an acid medium. Table II is an illustrative record of one of a set of 16 determinations of the rate of the unimolecular reaction in different solvents at different temperatures. Table III records the constants obtained in this set of measurements. In general, the initial concentration of *iso*propyl bromide was about $N/10$ in this series, and nothing else was added to the aqueous-alcoholic medium at the commencement of reaction. Expt. 13, however, shows the small medium effect obtained by increasing the initial concentration to $N/5$, and Expt. 14 illustrates the effect of adding sodium bromide initially in a concentration of $N/7$, the concentration of *iso*propyl bromide being once again the usual $N/10$. These two experiments are excluded in deriving the mean values of the rate constants (summarised later).

TABLE I.

Expt. 1. Comparison of rate in dilute alkaline and acid solution. Solvent: "60%" aqueous alcohol. Temp. 45·0°. Constants, k_1, in hours^{-1}.

Alkaline solution.

Initially: [$Pr^\beta Br$] ~ $N/5$; NaOH = $N/200$. Samples of 10 c.c. titrated. [$Pr^\beta Br$] in c.c. of 0·986 × $N/200$-HCl.

t (hrs.).	[$Pr^\beta Br$].	10^3k_1.
0·00	425·80	—
1·10	422·10	7·95
2·20	419·05	8·04
2·50	417·35	7·93
		Mean : 7·97

Acid solution.

Initially: [$Pr^\beta Br$] ~ $N/5$; NaOH = 0. Samples of 10 c.c. titrated. [$Pr^\beta Br$] in c.c. of 1·270 × $N/200$-NaOH.

t (hrs.).	[$Pr^\beta Br$].	10^3k_1.
0·00	321·80	—
1·00	319·30	7·83
2·25	316·55	7·37
3·25	314·30	8·49
		Mean : 7·90

TABLE II.

Expt. 16. Illustrating determination of unimolecular rate constant. Solvent: "60%" aqueous alcohol. Temp. 65·0°. Initially [$Pr^\beta Br$] ~ $N/10$ and [NaOH] = 0. Samples of 5 c.c. titrated. [$Pr^\beta Br$]′ = [$Pr^\beta Br$] as determined in c.c. of 1·109 × $N/50$-NaOH; k_1' = corresponding k_1 in hours^{-1}. [$Pr^\beta Br$]″ = [$Pr^\beta Br$] as determined in c.c. of $N/100$-$AgNO_3$; k_1'' = corresponding k_1 in hours^{-1}.

t (hrs.).	[$Pr^\beta Br$]′.	[$Pr^\beta Br$]″.	$10^2k_1'$.	$10^2k_1''$.	t (hrs.).	[$Pr^\beta Br$]′.	[$Pr^\beta Br$]″.	$10^2k_1'$.	$10^2k_1''$.
0·00	22·50	49·90	—	—	8·50	13·00	28·60	6·52	6·54
2·10	19·50	43·20	6·82	6·82	9·90	11·50	25·35	6·79	6·84
3·25	18·05	39·75	6·79	6·68	12·00	10·00	22·00	6·75	6·81
4·25	16·85	37·25	6·82	6·88	24·00	4·65	10·00	6·56	6·70
5·50	15·45	34·35	6·82	6·79	31·00	2·65	5·60	6·91	—
7·00	14·10	30·95	6·68	6·82			Means	6·75	6·76

TABLE III.

Expts. 11—26. Summary of first-order rate constants. Initially: [Pr$^\beta$Br] ~ $N/10$, [NaOH] = 0, and [NaBr] = 0 except in Expts. 13 and 14. k_1' and k_1'' are rate constants in hours^{-1} as determined by titration with NaOH and AgNO$_3$ respectively.

Solvent : " 60% " aqueous alcohol.

Expt.	Temp.	$10^2k_1'$.	$10^2k_1''$.
11	45·0°	0·798	0·804
12	,,	0·798	—
13 *	,,	0·745	—
14 †	,,	0·750	—
15	55·0	2·39	2·40
16	65·0	6·75	6·76
17	,,	6·74	—
18	75·0	17·5	17·6
19	,,	17·9	17·7

Solvent : " 80% " aqueous alcohol.

Expt.	Temp.	$10^2k_1'$.	$10^2k_1''$.
20	45·0°	—	0·278
21	,,	0·276	0·276
22	55·0	0·844	0·856
23	65·0	2·44	2·47
24	,,	2·42	2·42
25	75·0	6·59	6·50
26	,,	6·55	6·56

* Initial [Pr$^\beta$Br] = $N/5$.
† ,, [NaBr] = $N/7$.

Results for the Total Second-order Rate Constants.—Tables IV—VII relate to the total second-order rate constants (reactions S$_N$2 + E2) as calculated from the formula

$$k_2 = \{1/t(b-a)\}\log_e\{b(a-x)/a(b-x)\}, \text{ or } k_2 = x/ta(a-x) \text{ if } a = b,$$

after modification to allow for the simultaneous unimolecular reaction (above). Here b is the initial concentration of sodium hydroxide; a and x have already been defined. Table IV(A) illustrates the constancy of $\mathbf{k}_1$ and the drift of $\mathbf{k}_2$ when these " constants " are calculated by applying to the whole reaction in $N/50$-sodium hydroxide the integrated rate equations without correction for the fact that first- and second-order reactions are present together; $\mathbf{k}_1$ is nearly constant in this case because the proportion of second-order reaction is small. Table IV(B) shows the effect obtained when the same uncorrected equations are applied to the reaction in $N/10$-sodium hydroxide : here the proportion of the first-order reaction is small. In judging the drifts of the " constants " it must be borne in mind that in the first case only about 8% of the total amount of *iso*propyl bromide is consumed during the run, and in the second about 50%. Table V is an illustrative record of one of a set of 12 determinations of the true bimolecular rate constant for different solvents and temperatures. Table VI summarises the constants obtained in this series of experiments. Expt. 45 was a closely concordant duplicate of the initial part of Expt. 44, but is not recorded because it could not be completed owing to thermostat trouble. Table VII shows the effect of the concentration of sodium hydroxide on the bimolecular rate constants. The value obtained with an initial $N/10$-concentration of alkali is only approximate. Throughout all the experiments recorded in Tables IV—VII the initial concentration of *iso*propyl bromide was about $N/10$, and in the experiments of Table VI, the initial concentration of sodium hydroxide was about 0·85N; this rather high value was chosen in order that the reaction whose rate was sought should be the principal one, and it was maintained roughly constant throughout the series in order to standardise the activity effects to which the variations of rate exhibited in Table VII are ascribed.

TABLE IV.

Expts. 31, 32. Application of integrated rate equations to reaction in $N/50$- and $N/10$-sodium hydroxide. Solvent : " 60% " aqueous alcohol. Temp. 45·0°. Initially [Pr$^\beta$Br] ~ $N/10$. Samples of 5 c.c. titrated. [Pr$^\beta$Br] and [NaOH] expressed as equivalent c.c. of $N/200$-AgNO$_3$. $\mathbf{k}_1$ in hours^{-1}; $\mathbf{k}_2$ in l./g.-mol./hour.

(A) Initial [NaOH] ~ $N/50$.

t (hrs.).	[Pr$^\beta$Br].	[NaOH].	$10^2\mathbf{k}_1$.	$\mathbf{k}_2$.
0·00	100·00	21·50	—	—
1·00	98·75	20·25	1·27	2·18
2·02	97·50	19·00	1·26	2·26
3·00	96·30	17·80	1·26	2·35
4·00	95·20	16·70	1·23	2·37
6·50	92·50	14·00	1·20	2·51
7·25	91·70	13·20	1·20	2·57

(B) Initial [NaOH] ~ $N/10$.

t (hrs.).	[Pr$^\beta$Br].	[NaOH].	$10^2\mathbf{k}_1$.	$10\mathbf{k}_2$.
0·00	88·40	88·40	—	—
3·00	81·10	81·10	2·88	3·00
5·00	76·80	76·80	2·81	3·02
7·00	72·60	72·60	2·81	3·11
11·50	65·60	65·60	2·60	3·02
16·75	58·50	58·50	2·49	3·05
22·00	52·50	52·50	2·37	3·11
26·00	48·70	48·70	2·30	3·14
31·50	44·20	44·20	2·19	3·17

TABLE V.

Expt. 44. Illustrating determination of bimolecular rate constant. Solvent: "80%" aqueous alcohol. Temp. 50·0°. Initially [$\text{Pr}^{\beta}\text{Br}$] ~ $N/10$; [NaOH] ~ 0·8N. Samples of 5 c.c. titrated. [$\text{Pr}^{\beta}\text{Br}$] and [NaOH] expressed in c.c. of $N/100$-silver nitrate. $\mathbf{k}_2$ is the uncorrected bimolecular "constant" in l./g.-mol./hour. "Corr. k_1" signifies the correction to be applied to $\mathbf{k}_2$ in order to allow for the unimolecular reaction. k_2 is the corrected constant in l./g.-mol./hour.

t (hrs.).	[$\text{Pr}^{\beta}\text{Br}$].	[NaOH].	$\mathbf{k}_2$.	"Corr. k_1."	k_2.
0·00	46·00	399·00	—	—	—
0·35	43·20	396·20	0·226	0·006	(0·220)
1·00	37·70	390·70	0·252	0·006	0·246
1·50	34·35	387·35	0·248	0·006	0·242
2·25	29·70	382·70	0·249	0·006	0·243
3·10	25·60	378·60	0·244	0·006	0·238
4·00	21·60	374·60	0·245	0·006	0·239
5·05	17·80	370·80	0·246	0·007	0·239
6·05	14·40	367·40	0·253	0·007	0·246
8·50	9·70	362·70	0·243	0·007	0·236
					Mean : 0·241

TABLE VI.

Expts. 36—47. Summary of bimolecular rate constants. Initially [$\text{Pr}^{\beta}\text{Br}$] ~ $N/10$ and [NaOH] ~ 0·85N. k_2 is in l./g.-mol./hour.

Solvent : "60%" aqueous alcohol.						*Solvent : "80%" aqueous alcohol.*		
Expt.	Temp.	k_2.	Expt.	Temp.	k_2.	Expt.	Temp.	k_2.
36	45·0°	0·1060	40	60·0°	0·485	44	50·0°	0·241
37	,,	0·1068	41	,,	0·490	46	80·0	4·64
38	60·0	0·483	42	,,	0·488	47	,,	4·57
39	,,	0·487	43	75·0	2·000			

TABLE VII.

Expts. 41—44. Variation of bimolecular rate constant with initial [NaOH]. Solvent: "60%" aqueous alcohol. Temp. 45·0°. Initial [$\text{Pr}^{\beta}\text{Br}$] ~ $N/10$.

Initial [NaOH], g.-mol./l.	0·1	0·2	0·5	1·0
k_2, l./g.-mol./hr.	0·183	0·169	0·134	0·106

Results for the Ratio of the Separate Second-order Rates.—Table VIII exemplifies results establishing the point that the olefin elimination is a bimolecular reaction, because the amount of olefin formed is a constant fraction of the total bimolecular reaction, independently of the time during a run or of the initial concentrations of alkali in different runs. The table shows in successive columns the initial concentration of alkali, the proportion of the total possible reaction which had actually occurred when the sample was taken for the estimation of olefin, and the extents to which the various constituent reactions have taken place at the same time, these quantities being in every case expressed as percentages of the total actual reaction at the time in question. The figures in col. 3 are derived by calculation from the first- and second-order constants, using the formulæ given above; those in col. 4 follow by difference. The data in col. 5 are observations of the yield of olefin; those in col. 6 follow by difference. Cols. 7 and 8 show the fractions in which the total actual bimolecular reaction is partitioned between the substitution and olefin elimination. Their constancy shows that they represent the ratios in which the total second-order rate constants have to be split up to give the rate constants for the bimolecular substitution and the elimination. It is also clear that in order to obtain these ratios it is not necessary to estimate olefin at various times throughout the progress of reaction: estimations made with the product of the completed reaction should suffice if the first- and second-order rate constants are known. Utilising this result, a series of experiments were made to determine the percentage of olefin formed in the completed reaction in various solvents and at various temperatures: the data obtained are in Table IX. Col. 4 gives the observed percentages, each of which represents the mean of four observations, of propylene, col. 5 the calculated percentage of products formed by the unimolecular reaction, and col. 6 the figures, obtained by difference, for the products formed by the bimolecular reaction. The last two cols. contain the factors which, when multiplied into the total second-order rate constants, will give the rate constants for the two separate bimolecular reactions.

TABLE VIII.

Expts. 51—54. Constancy of the ratio of olefin formed to the total second-order reaction. Solvent : " 60% " aqueous alcohol. Temp. 60°. Initial [Pr$^\beta$Br] ~ $N/10$.

Initial [NaOH].	Actual/ possible reaction.	S_N1 (%). (calc.).	$S_N2 + E2$ (%) (total 2nd order).	E2 (%) (obs.).	S_N2 (%) (diff.).	$\frac{S_N2}{S_N2 + E2}$.	$\frac{E2}{S_N2 + E2}$.
0·940	0·373	8·25	91·75	50·0	41·75	0·455	0·545
,,	0·607	8·35	91·65	49·9	41·75	0·456	0·544
,,	1·000	8·40	91·6	50·9	40·7	0·444	0·556
0·465	1·000	14·50	85·5	47·9	37·6	0·440	0·560

TABLE IX.

Expts. 61—67. Proportion of olefin formed in completed reactions. Initial [Pr$^\beta$Br] ~ $N/10$. Initial [NaOH] ~ 0·85N.

Expt. No.	Solvent.	Temp.	E2 (%) (obs.).	S_N1 (%) (calc.).	S_N2 (%) (diff.).	$\frac{S_N2}{S_N2 + E2}$.	$\frac{E2}{S_N2 + E2}$.
61	" 60% " aqueous alcohol	45·0°	48·73	8·38	42·89	0·468	0·532
62		60·0	50·78	8·92	40·30	0·443	0·557
63		75·0	52·45	9·03	38·52	0·424	0·575
64		100 *	56·85	10·68 †	32·47	0·364	0·636
65	" 80% " aqueous alcohol	50·0	56·76	2·59	40·65	0·419	0·581
66		80·0	59·40	2·90	37·70	0·388	0·612
67		100 *	64·46	3·15 †	32·39	0·335	0·665

* Temperature maintained by boiling water-bath only, and not accurately controlled.

† As k_1 and k_2 were not measured for this temperature, the values necessary for the calculation were obtained by extrapolation using the Arrhenius formula.

Mean Values and Temperature Coefficients of Rate Constants.—Table X(*a*) shows the mean values of the unimolecular rate constants, k_1 (reaction S_N1), for the solvents and temperatures investigated, together with energies of activation calculated from the formula $k_1 = Be^{-E/RT}$; k_1 and B are in hours^{-1} and E in cals. Table X(*b*) contains similar data relating to the total bimolecular rate constants, k_2 (reactions $S_N2 + E2$), the energies of activation being calculated from the formula $k_2 = Be^{-E/RT}$; k_2 and B are in l./g.-mol./hour. Table X(*c*) refers to the bimolecular substitution (reaction S_N2); the rate constants, k_2, are obtained by decomposing the bimolecular rate constants of Table X(*b*) in accordance with the factors given in Table IX. Table X(*d*) exhibits similarly obtained rate constants, k_2, for the elimination (reaction E2). In Tables X(*c*) and X(*d*) the temperature coefficients are expressed as Arrhenius critical energies calculated from equations of the form given above. In Table XI we summarise the formulæ expressing the rate constants of the several reactions, and in order to facilitate comparison we give also the calculated rate constants for 50°.

TABLE X.

(*a*) *Reaction* S_N1.

	Rate constants.			Temp. coeff.	
Temp.	" 60% " EtOH. k_1.	" 80% " EtOH. k_1.	Temps.	" 60% " EtOH. E.	" 80% " EtOH. E.
45·0°	0·00800	0·00277	45—55°	22,750	23,210
55·0	0·0240	0·00850	55—65	22,760	23,130
65·0	0·0675	0·0244	65—75	22,520	23,160
75·0	0·0177	0·0655	45—65	22,760	23,160
			55—75	22,650	23,140
			45—75	22,690	23,170

(*b*) *Reactions* $S_N2 + E2$.

	Rate constants.			Temp. coeff.	
Temp.	" 60% " EtOH. k_2.	" 80% " EtOH. k_2.	Temps.	" 60% " EtOH. E.	" 80% " EtOH. E.
45·0°	0·1064	—	45—60°	21,300	—
50·0	—	0·241	60—75	21,670	—
60·0	0·487	—	45—75	21,490	—
75·0	2·000	—	50—80	—	22,250
80·0	—	4·600			

(*c*) *Reaction* S_N2.

	Rate constants.			Temp. coeff.	
Temp.	k_2.	k_2.	Temps.	E.	E.
45·0°	0·0498	—	45—60°	20,560	—
50·0	—	0·101	60—75	20,960	—
60·0	0·216	—	45—75	20,760	—
75·0	0·849	—	50—80	—	21,700
80·0	—	1·79			

(*d*) *Reaction* E2.

	Rate constants.			Temp. coeff.	
Temp.	k_2.	k_2.	Temps.	E.	E.
45·0°	0·0566	—	45—60°	21,950	—
50·0	—	0·140	60—75	22,250	—
60·0	0·271	—	45—75	22,100	—
75·0	1·153	—	50—80	—	22,640
80·0	—	2·81			

TABLE XI.

Summary of formulæ expressing rate constants.

(k_1 in hours; k_2 in l./g.-mol./hour.)

Reaction.	" 60% " Aqueous alcohol.	" 80% " Aqueous alcohol.
S_N1	$\log_e k_1 = 31{\cdot}18 - 22{,}690/RT$ $k_1^{50°} = 0{\cdot}0148$	$\log_e k_1 = 30{\cdot}79 - 23{,}160/RT$ $k_1^{50°} = 0{\cdot}00482$
S_N2	$\log_e k_2 = 29{\cdot}88 - 20{,}760/RT$ $k_2^{50°} = 0{\cdot}082$	$\log_e k_2 = 31{\cdot}55 - 21{,}700/RT$ $k_2^{50°} = 0{\cdot}101$
E2	$\log_e k_2 = 32{\cdot}13 - 22{,}100/RT$ $k_2^{50°} = 0{\cdot}097$	$\log_e k_2 = 33{\cdot}34 - 22{,}640/RT$ $k_2^{50°} = 0{\cdot}140$
S_N2 + E2	$\log_e k_2 = 31{\cdot}80 - 21{,}490/RT$ $k_2^{50°} = 0{\cdot}179$	$\log_e k_2 = 33{\cdot}28 - 22{,}250/RT$ $k_2^{50°} = 0{\cdot}241$

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