**188.** *Mechanism of Substitution at a Saturated Carbon Atom. Part XXIII. A Kinetic Demonstration of the Unimolecular Solvolysis of Alkyl Halides. (Section E) A General Discussion.*

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In this paper the considerations outlined in the abstract on p. 960 are made quantitative and the experimental observations of the preceding four papers are reviewed on this basis. The result is to establish unequivocally the existence, nature, and general importance of the unimolecular mechanism of both solvolytic and non-solvolytic substitutions, and to provide a somewhat detailed picture of its manner of working, especially in relation to the life history of the carbonium ion. A summarising statement of these conclusions is given on pp. 1003–1008 : they cohere excellently with the conclusions that have been derived from the effect of changes in the compound substituted, in the substituting agent, and in the solvent on the rate and course of substitution, and from the associated stereochemical phenomena (cf. pp. 1008–1011).

In this paper we discuss collectively the material presented in the four preceding papers. The problem is the determination of the mechanism of those nucleophilic substitutions in which the substituting agent is the solvent, the example being the hydrolysis of alkyl halides in aqueous acetone. All the halides now investigated are of a type for which we have previously concluded, from quite different evidence, that the mechanism of their hydrolysis in aqueous solvents is unimolecular. We propose later to publish a corresponding investigation on halides for which the previous conclusion has been that their aqueous hydrolysis is bimolecular.

In order to show the relation of this part of our work to the whole section which deals with solvents as substituting agents, we give a list of the methods which have now been used to determine mechanism in solvolytic substitutions :

(1) From the kinetic form of the substitution reaction.

(2) From the effect of structural changes in the compound substituted on the reaction rate.

(3) From the effect of systematic changes in the substituting agent on the reaction rate.

(4) From the effect of solvent changes on the reaction rate and on the products.

(5) From the effect of salt additions on the reaction rate and on the products.

(6) From the stereochemical course of the substitution.

The original theory (Hughes, Ingold, and Patel, J., 1933, 526) provided only two methods, nos. (2) and (3), and for some years these remained the only available methods. Cowdrey, Hughes, Ignold, Masterman, and Scott then added method (6) (J., 1937, 1252); and Bateman, Hughes, and Ingold, method (4) (J., 1938, 881). The present group of papers completes the list by developing and applying methods (1) and (5).

### (1) *Preliminary Qualitative Considerations.*

We have stated in the past that method (1), the direct kinetic method, is unavailable for solvolytic substitution, because, with the solvent as reagent, both the bimolecular and the unimolecular mechanism require first-order kinetics; and this is true in certain cases, provided one is thinking only of the rough fitting of the kinetics to the conventional first- or second-order rate-laws. From a more precise point of view, it is still true that, with a well-buffered solvent concentration, a bimolecular substitution should follow the first-order rate-law to a very close approximation. On the other hand, a unimolecular substitution should in principle exhibit deviations, which need not be small, from the first-order rate-law, owing, as we pointed out in the preliminary paper (this vol., p. 960), to the growth of ionic re-association during reaction :

$$\text{RCl} \underset{(2)}{\overset{(1)}{\rightleftharpoons}} \text{R}^+ + \text{Cl}^- \xrightarrow[\text{H}_2\text{O}]{(3)} \text{ROH} + \text{H}^+ + \text{Cl}^-$$
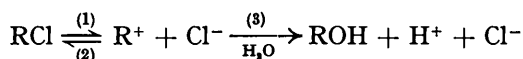
As larger halide-ion concentrations are built up by reaction (3), reaction (2) gains in importance, so that the rate-determining ionisation becomes progressively retarded by its reversibility, without causing any reversal of the stoicheiometric reaction, which may be a completely irreversible hydrolysis. This characteristic deviation from first-order kinetics has been detected; indeed, in chosen examples, it was large enough to change the kinetic form completely; and we shall show that the detected disturbance is correctly identified. The bimolecular mechanism provides for no such effect in a stoicheiometrically irreversible hydrolysis.

The development of method (5) is based on quite analogous considerations. There are three principal cases : (i) The first case is that in which we add a salt (*e.g.*, NaCl) whose anion is identical with that formed from the alkyl halide (*e.g.*, RCl). In the unimolecular mechanism, the added anion can retard hydrolysis by reversing the ionisation, without reversing the hydrolysis itself. This highly characteristic effect has been observed. The bimolecular mechanism provides for no such retardation in irreversible hydrolysis. (ii) In the second case, the anion of the added salt (*e.g.*, NaBr) is such that the alkyl derivative which it might form (*e.g.*, RBr) is much more rapidly hydrolysed than the original alkyl halide (*e.g.*, RCl). The unimolecular mechanism now demands no change of initial rate, which still is identical with the rate of ionisation of the alkyl halide, but requires only a lessening of the growing retardation discussed in the preceding paragraph. The bimolecular mechanism, however, requires acceleration throughout the course of reaction, the acceleration depending directly on the extent to which the added anion attacks the alkyl halide molecule. (iii) In the third case, the anion of the added salt (*e.g.*, $NaN_3$) is such that the corresponding alkyl derivative (*e.g.*, $RN_3$) is not hydrolysed. The conclusions concerning the total rate of destruction of the alkyl halide (*e.g.*, RCl) are the same as in the preceding case. However, there are now two final products (*e.g.*, ROH and $RN_3$), and another important matter is the correlation of their proportions with the rate changes. The principle involved is identical with that which Bateman, Hughes, and Ingold applied to the use of mixtures of reactive solvents (such as water and alcohol) in order to determine mechanism. In the unimolecular mechanism the products are formed in reaction-stages other than that whose rate we measure, and therefore there should be no connexion between the proportions of products and the measured rate. In the bimolecular mechanism on the other hand, there is only one reaction-stage, so that the reactions in which the products are formed contribute additively to the measured rate; thus there is a definite and simple relation between the proportions of products and the measured, total rate. A further criterion can be based on a comparison of the proportions of products as between one halide and another. If two different alkyl halides have the same alkyl group, the unimolecular mechanism requires that the proportions in which the products are formed should be the same; because the products are formed from the alkyl cation, and the cation is the same. According to the bimolecular mechanism, we should not necessarily expect any connexion. All these requirements of mechanism are later examined more fully and compared with the experimental findings.

The above consequences of mechanism, both those concerning the kinetic form of hydrolysis, and those relating to salt effects on reaction rate and product composition, derive from the mass-law : superposed on them all there is the activity effect arising from the ionic strengths of the solutions. We consider only small ionic strengths, and refer first to the kinetic form of hydrolysis in the absence of salts (method 1). The qualitative picture of the ionic strength effect is very similar to that by which we explained solvent effect (Hughes and Ingold, J., 1935, 252). Just as in the unimolecular ionisation of a neutral molecule, or the bimolecular substitution of a neutral molecule by a neutral reagent, an increase in the solvating power of the solvent accelerates, because, whilst the initial state is not much affected, the transition state with its quasi-ionic charges can better stabilise itself by attracting solvent dipoles, so also, in the same reactions, an increase of ionic strength will accelerate because the transition state charges can better stabilise themselves by collecting suitable ionic atmospheres. Again, just as the solvent effect is much greater in unimolecular than in bimolecular substitution, because of the greater diffusion of charges in the transition state of the latter, so also, and for the same reason, we expect

the accelerating effect due to an increase of ionic strength to be much more marked in the unimolecular substitution of a neutral molecule than in the bimolecular substitution of the same molecule by a neutral reagent.   Since the ionic strength increases in the course of a solvolytic substitution of a neutral molecule such as an alkyl halide, we expect a progressive increase in the instantaneous first-order rate constant, superposed, if the mechanism is unimolecular, on a progressive decrease due to the operation of the mass-law.   If the mechanism is bimolecular, we expect a considerably smaller rise in the instantaneous specific rate, superposed on the constant first-order rate obtaining under the mass-law.   The effects expected from the unimolecular mechanism have been observed.   The ionic strength effect is also expected, as we shall show presently, to diminish with increasing water-content of the aqueous acetone solvent : this solvent effect has also been observed.

Turning now to the influence of ionic strength on the effect of added salts (method 5), the important point is that, in unimolecular substitution, *all* ionised salts should, so far as this factor is concerned, strongly increase the ionisation rate, and therefore increase the measured total rate of elimination of halide ion from the alkyl halide : salts having an anion in common with that formed from the alkyl halide are not an exception.   Indeed, we shall give reason for believing that all uni-univalent salts should accelerate the same reaction, in the same solvent at the same temperature, to the same extent in limiting dilutions, though at practical dilutions there may be appreciable differences between one salt and another.   The ionic strength acceleration should, of course, be superposed on the mass-law retardation in the case of salts having an anion identical with that given by the alkyl halide, but for all other salts should be the sole effect on the initial rate of elimination of halide ion from the alkyl halide.   In the bimolecular mechanism the ionic strength effect of added salts should result in a small acceleration of hydrolysis, which should be the sole effect in the case of salts having the same anion as that given by the alkyl halide, but should be superposed on the mass-law acceleration of the total substitution for other salts. The effects arising from the unimolecular mechanism have all been observed, together with the theoretically expected decrease of the ionic strength effects in more aqueous solvents.

In order to assist the recollection of these (collectively rather complicated) qualitative considerations, the main points are gathered together in Table I.   It should be emphasised that they apply to dilute solution; in concentrated salt solutions, for example, quite complicated factors might influence the rate in ways for which no reasonably precise theory can at present be provided.   The term " specific rate," as used here and throughout this paper, means the instantaneous first-order rate constant, *viz.* $(dx/dt)/(a - x)$.

TABLE I.

*Predicted Qualitative Effects.*

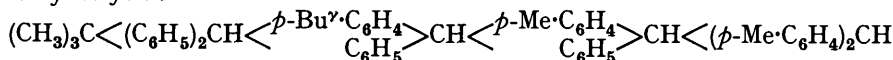| Mechanism. | Method. | Ionic strength effect.* | + | Mass-law effect. |
|---|---|---|---|---|
| $S_N1$ | (1) Kinetic form | Progressive rise of specific rate | + | *Progressive fall* of specific rate |
| | (5) Salt effects | Acceleration | | { + *Retardation* (" common-ion " salts) <br> { + No effect† (other salts) |
| $S_N2$ | (1) Kinetic form | Small progressive rise of specific rate | + | No effect |
| | (5) Salt effects | Small acceleration | | { + No effect (" common-ion " salts) <br> { + Acceleration ‡ (other salts) |

* These effects must all diminish with increasing water content of the solvent.

† No effect on the *initial* rate of liberation of halide ions, *i.e.*, no effect before the " progressive fall of specific rate," due to the mass-law effect of the liberated halide ions, sets in.   The added salts, however, modify the mass-law effect of these anions.

‡ This acceleration must agree with the product composition when the product given by intervention of the added salt is stable.

As stated above, we have worked with alkyl halides of a type for which the mechanism of aqueous hydrolysis has, from other evidence, been previously concluded to be unimolecular.   It was our object to seek the mass-law effect, especially the two retardations indicated by the italics in the above Table; but we realised that we could never get rid of superposed ionic strength effects.   From our study of the stereochemical course of

substitution (method 6) we had arrived at a picture of unimolecular solvolytic substitution, which will be made more definite in the sequel; and this led us to the (partly intuitive) prediction that, whilst the ionic strength effect would apply universally to those alkyl halides which are hydrolysed by the unimolecular mechanism, the mass-law effects should increase with the stability of the organic cation which is formed in the course of unimolecular substitution. It is a question of the length of life of this cation : within limits, the longer the time interval between the consecutive stages of unimolecular substitution the more prominent should be the mass-law effects. Therefore we set up the following alkyl series as illustrating a progressive increase in the stability of the cations of those alkyl groups whose investigated halides are believed to react by the unimolecular mechanism in aqueous hydrolysis :

$$(CH_3)_3C < (C_6H_5)_2CH < \frac{p\text{-}Bu^\gamma \cdot C_6H_4}{C_6H_5} > CH < \frac{p\text{-}Me \cdot C_6H_4}{C_6H_5} > CH < (p\text{-}Me \cdot C_6H_4)_2CH$$

The evidence for this series is partly theoretical and partly empirical. The theoretical basis is as follows : (a) An α-phenyl group must strongly increase the stability of the cation owing to mesomerism. (b) A *p*-alkyl group must further increase stability because of the energy effect associated with the electron repulsion of alkyl groups attached to unsaturated carbon systems (a form of resonance; this vol., p. 909). (c) A *p*-methyl group will be the most effective *p*-alkyl group in systems which, like these cations, have a very strong electron affinity, because the CH-conjugation creates further resonance energy (this vol., p. 949). The only direct empirical evidence is the knowledge (Cowdrey *et al.*, *loc. cit.*) that the introduction of an α-phenyl substituent into an alkyl group R having α-asymmetry increases the racemisation accompanying the unimolecular substitution of optically active RX : the increase implies an increased length of life of the intermediate cation R$^+$. However, there is also indirect evidence. Since the same factors of stability that we can introduce, as explained above, into the fully formed cations must already be partly effective in the transition states of ionisation, there should be a parallel between the rates of these similar processes and the stabilities of their ionic products; and as, independently of this work, we have evidence that the rates of aqueous hydrolysis of the alkyl halides considered measure their rates of ionisation, we can adduce the rates themselves as evidence for our series. We deal with the difficulty of knowing at this stage in what form to quote the rates in view of the deviations from classical kinetic laws by utilising the conclusion, made definite later, that the *initial* first-order rate constants represent rates of ionisation. These initial rates are collected in Table II, the experimental material on which they are based being recorded in various accompanying papers. It will be seen that, for given physical conditions and the same halogen atom, the rates vary with the alkyl group in a manner which supports our series.

TABLE II.

*Initial First-order Rates* $[10^5 k_1^{(0)}$ *with* $k_1^{(0)}$ *in* $sec.^{-1}]$ *of Hydrolysis of Alkyl Halides.*

| Aqueous acetone. | Temp. | Bu$^\gamma$ bromide. | Ph$_2$CH bromide. | Ph$_2$CH chloride. | Bu$^\gamma$·C$_6$H$_4$·CHPh chloride. | Me·C$_6$H$_4$·CHPh chloride. | (Me·C$_6$H$_4$)$_2$CH chloride. |
|---|---|---|---|---|---|---|---|
| "90%" | 0° | — | — | — | — | — | 9·10 |
| | 25 | 1·27 | — | 0·460 | — | 9·46 | — |
| | 50 | 19·0 | 201 | 5·80 | 55·0 | — | — |
| "85%" | 0 | — | — | — | — | — | 47·0 |
| "80%" | 0 | — | — | 0·282 [1] | 3·59 [2] | 8·35 [3] | 160 |
| | 25 | — | — | 7·24 [4] | 76·0 [5] | 160 [6] | — |
| "70%" | 25 | 51·5 | — | 32·0 | — | — | — |

[1] Hughes, Ingold, and Taher (this vol., p. 949), 0·282.   [2, 3] Quoted from H., I., and T.
[4] H., I., and T., 7·28.*   [5] H., I., and T., 79·6.*   [6] H., I., and T., 156.*

[* It will be understood that, as the rates of these reactions are very sensitive to solvent composition, it is difficult always to secure exact agreement with earlier experiments, in which different batches of solvent, possibly of very slightly different composition, were employed. In all work in which a precise comparison of rates is desired, it has been our practice to take the medium from a single stock.]

We expect, then, to find ionic strength effects throughout this series of alkyl groups, whilst, if the mechanism is unimolecular, the superposed mass-law effects, which in this

event are highly characteristic, should be developed with increasing prominence as we pass towards the right-hand members. The investigation of the left-hand members is necessary because here we observe the ionic strength effects in their most nearly pure form, thus establishing a basis from which the superposed mass-law effects can be assessed when towards the right hand end of the series they make the dominating contribution.

### (2—3) *Kinetic Form of Hydrolysis (Method 1).*

(2) *Effect of Ionic Strength alone on the Kinetics of Hydrolysis.*—(a) *Kinetic form of hydrolysis for a single solvent.* In the immediate sequel we shall follow up the consequences of supposing the mechanism of hydrolysis to be unimolecular. A similar discussion could be given for the bimolecular mechanism, but it would be difficult to carry it quite so far quantitatively. The qualitative differences between the two mechanisms in relation to the ionic strength effect have already been pointed out.

Using the formalism of Polanyi, Evans, and Eyring (cf. Polanyi, J., 1937, 629), we represent the rate of ionisation of RX as the product of a transit frequency through, and the instantaneous population of, the transition state. Taking $dl$ as the " thickness " of the state, the former factor is written $v/dl$, where $v$ is the thermal velocity along $dl$. The population of ionising particles in the transition state, $\frac{1}{2}c_T$ per unit volume of real space, is defined by an infinitesimal " equilibrium constant " $dK_c = \omega_c dl = c_T/c_{RX}$, so that the rate equation becomes $- dc_{RX}/dt = \frac{1}{2}v\omega_c c_{RX}$. But $dK_c$ is not a true constant for the " equilibrium," and we therefore define one, as follows :

$$dK_a = a_T/a_{RX} = a_T/c_{RX} = f_T(c_T/c_{RX}) = f_T\omega_c dl = \omega_a dl$$

Here the $a$'s with subscripts denote activities, and $f_T$ represents the activity coefficient of the transition state; and the approximation is made that this differs from unity by so much more than does the activity coefficient of RX that the latter may be set equal to unity in these equations. It follows that

$$- dc_{RX}/dt = \frac{1}{2}v\omega_a c_{RX} f_T^{-1} = k_1^{(0)} c_{RX} f_T^{-1} \quad . \quad . \quad . \quad . \quad (1)$$

where $k_1^{(0)}$ is the first-order rate constant for zero ionic strength.

We have now to calculate the activity coefficient $f_T$ for the transition state of ionisation. We know that when the conception of the transition state is applied to bimolecular reactions it leads to Brönsted's rate equation; that this equation contains the activity coefficient of the transition state; and that this activity coefficient is always taken to be determined by the charge on the transition state, just as though the latter were a permanent structure. The applications of Brönsted's equation form a remarkable instance of the success of equilibrium theory outside the range of its logical validity, and, guided by this known experience, we calculate the activity coefficient for our transition state by treating it as a permanent dipole. The principle involved is the same as in Debye's theory of the activity coefficient of an ion, *viz.*, that the surrounding ions will reduce the magnitude of the electrical potential of the central charge (of each of the dipole charges in our case), thus stabilising the system, or, in other words, reducing its free energy and activity.

For our present purpose, the simplest model of the transition state is that of two point charges $\pm ze$ separated by a fixed distance $d$, and surrounded by a dilute atmosphere of point-ions of charges $\pm e$. The Debye–Poissan equation for the potential $\psi$ at a point due to *any* central electrical distribution in a dilute atmosphere of univalent ions is

$$\Delta^2\psi = \kappa^2\psi \quad \text{with } \kappa^2 = 8\pi ne^2/DkT,$$

where $n$ is the number of ions of either sign per c.c., $D$ is the dielectric constant of the solvent, $k$ is Boltzmann's constant and $T$ is the absolute temperature. We have to find the solution appropriate to a central dipole. The differential equation is separable in polar co-ordinates, and, for an external point of co-ordinates $r$, $\theta$, $\phi$ with respect to the centre of the dipole as origin and the dipole axis as polar axis, the solution is found to be

$$\psi = \frac{zed}{D} \cdot \frac{1}{r^2}(1 + \kappa r)e^{-\kappa r} \cdot \cos \theta$$

3 U

The potential due to the ionic atmosphere alone at either of the central $\pm$ charges reduces to

$$\psi_{\text{atmosphere}} = \mp \tfrac{1}{2}\kappa^2 zed/D,$$

from which, by the usual process of discharging the ions at finite dilution and recharging them at infinite dilution, it follows that

$$-\ln f_T = \frac{4\pi}{1000} \cdot \frac{Ne^4}{k^2} \cdot z^2 d \cdot \frac{\mu}{(DT)^2} \quad . \quad . \quad . \quad . \quad (2)$$

where $N$ is Avogadro's number, and $\mu$ is the ionic strength of the solution, *i.e.*, the concentration of the uni-univalent electrolyte. It will be noted that the logarithm of the activity coefficient of the dipole depends on $\mu/(DT)^2$, not on $\mu^{\frac{1}{2}}/(DT)^{3/2}$ as does the logarithm of the activity coefficient of an ion. The law is only a limiting one, but we may expect it to hold over a rather larger concentration range than does the corresponding law for ions, because of the smaller density variations of the ionic atmosphere around dipoles. It contains one unknown constant, $\sigma = z^2 d$, of the dimensions of length (for $z$, the transferred charge, reckoned as a fraction of the electronic charge, is dimensionless). This constant must, of course, be determined from the rate data.

We report this calculation in outline only, because a more detailed treatment of the problem of the activity coefficient of a zwitterion has since been made available by Kirkwood (*Chem. Rev.*, 1939, **24**, 233). He placed the dipole charges either one at each focus, or both close together on the axis of symmetry near one focus, of a prolate spheroidal " molecule " of variable eccentricity. His formulæ are consistent with ours, but are much more complicated and less suited to our particular applications. However, his investigation has been of value to us, because it has shown that the essential effect of molecular shape and charge disposition, within the range of his examination of these variables, is simply on a numerical constant, whose variation from our numerical constant we can regard as absorbed into our disposable length parameter, $\sigma$. He also made a partial examination of the effect of image forces, and showed that they increased the dependence of the activity coefficient on $DT$; however, numerical computation shows that this effect is of minor importance except for very bulky zwitterions.

In order to complete the derivation of our rate law, we have only to combine equations (1) and (2), inserting the values of the universal constants. Replacing $c_{RX}$ by the more usual $a - x$, and noting that, in the absence of added salts, the ionic strength $\mu$ is simply $x$, we obtain

$$dx/dt = k_1^{(0)}(a - x)\ \text{antilog}_{10}\ (0.912 \times 10^{16}\ \sigma x/D^2T^2) \quad . \quad . \quad . \quad (3)$$

Of the hydrolyses studied, that of *tert.*-butyl bromide is expected to exhibit the ionic strength effect with the least disturbance from mass-law effects. We may take the hydrolysis of $0.1056$M-*tert.*-butyl bromide in " 90% " aqueous acetone at $50°$ in the absence of added salts as a first illustration.* The data have been recorded (this vol., p. 960) in the form of integrated first-order rate constants,

$$\bar{k}_1 = 2.303 t^{-1} \log_{10}\{a/(a - x)\} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

(the bar signifies integration), and by combining this equation with the appropriate specialisation of equation (3), *viz.*,

$$dx/dt = k_1^{(0)}(a - x)\ \text{antilog}_{10}\ (1.806 \times 10^8 \sigma x),$$

we can, after a numerical integration of the latter, calculate the proportional change in the rate constant, $\bar{k}_1/k_1^{(0)}$, as a function of the percentage progress of reaction, $100x/a$, for any assumed value of $\sigma$.

The order of magnitude of $\sigma = z^2 d$ is not in doubt. Suppose, as an approximation, that

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* A small proportion of what is here called " hydrolysis " really consists in the formation of *iso*-butylene; but this does not affect the argument, because our analytical measurement includes the olefin production, and it is the *total* rate thus measured that represents the rate of ionisation of the alkyl halide, according to the mechanism underlying the calculation we are testing.

in the transition state of ionisation the equivalent of half an electron is transferred from carbon to bromine ($z = 0.5$), and that the whole of the positive charge is borne by the tertiary carbon atom. We require to know the length, $d$, to which the C–Br bond becomes stretched in the transition state, and can estimate this from the energy of activation and Morse's potential energy function; for, disregarding the small corrections due to zero-point energy in the ground state and resonance and tunnelling in the transition state, it will be at the energy of the activated state that the Morse curve cuts the potential energy curve for the ion-pair. In the Morse function we have taken the dissociation energy as 62 kg.-cals./g.-mol., the equilibrium C–Br separation as 2·05 A., and the force constant of the C–Br stretching vibration as $2.61 \times 10^5$ dynes/cm. For the energy of activation of ionisation we have taken the value, 23 kg.-cals./g.-mol., found for solvolysis in " 80% " aqueous alcohol (this vol., p. 925). The length of the stretched bond is then found to be 2·59 A. Thus $\sigma = 0.25 \times 2.59$ A. $= 0.65 \times 10^{-8}$ cm. It must be emphasised that this is only an order-of-magnitude calculation. When we selected the value of $\sigma$ which best fitted our results for the kinetics of the hydrolysis of *tert.*-butyl bromide in " 90% " aqueous acetone at 50°, we arrived at the value, $\sigma = 0.74 \times 10^{-8}$. The agreement is evidence for the unimolecular mechanism, since the ionic strength effect in the bimolecular mechanism is likely to be much smaller (Table I) than that calculated by the methods illustrated.

FIG. 1.

*Ionic Strength Effect.*
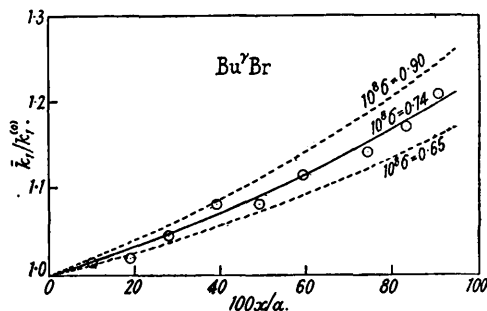


Hydrolysis of 0·1056M-*tert.*-butyl bromide in " 90% " aqueous acetone at 50°.
(Three theoretical curves and the experimental points.)

Fig. 1 shows three curves of the relation between $\bar{k}_1/k_1^{(0)}$ and $100x/a$, as calculated from equations (3) and (4) with constants $a$, $D$, and $T$ appropriate to the experiment under consideration, and different assumed values of $\sigma$. The agreement of the experimental points with the central curve is our first evidence that the progressive acceleration of the specific rate is essentially an ionic strength effect.

(b) *Temperature and solvent effects on the kinetic form of hydrolyses.* If we are correct in identifying the progressive acceleration as a nearly pure ionic strength effect, then the whole influence of temperature and solvent composition on the deviations from first-order kinetics should be summarised in the factor $D^{-2}T^{-2}$ contained in the argument of the anti-logarithm of equation (3). By adding more water to the aqueous acetone, we increase the dielectric constant considerably, and thus the whole antilogarithmic factor expressing the ionic strength effect on the kinetic form of hydrolysis will diminish towards unity. Temperature is similarly involved, although it is less easy to make proportionately considerable variations of the absolute temperature in kinetic measurements.

To test these predictions we carried out two hydrolyses at 25°, one in " 90% " and the other in " 70% " aqueous acetone; the initial concentrations, $a$, of *tert.*-butyl bromide were nearly the same as before, 0·1039 in the first case and 0·1049 in the second (this vol., p. 960). The appropriate specialisations of equation (3) are respectively

$$dx/dt = k_1^{(0)}(a - x) \text{ antilog}_{10}(1.644 \times 10^8 \sigma x)$$

and
$$dx/dt = k_1^{(0)}(a - x) \text{ antilog}_{10}(0.689 \times 10^8 \sigma x);$$

but now $\sigma$ is no longer disposable, having already been determined to be $0.74 \times 10^{-8}$. Thus we can calculate two completely determinate theoretical curves for the variation of $\bar{k}_1/k_1^{(0)}$ with $100x/a$.

These curves are in Fig. 2, together with the observations. It is obvious that our formulæ represent the solvent effect correctly, and this confirms our identification of the deviations from first-order kinetics as an ionic strength effect essentially.

(3) *Combined Mass-law and Ionic-strength Effects on Kinetic Form of Hydrolysis.*— (a) *Hypothetical case of mass-law effects acting alone.* As explained in Section (1) (cf. Table I), mass-law effects are peculiar to the unimolecular mechanism, and do not arise under the bimolecular mechanism; hence only the former mechanism requires to be considered in this section.

For polar reactions involving ions either as factors or as products, simple mass-law effects, undisturbed by ionic-strength effects, cannot be realised. Thus a consideration of mass-law effects alone cannot lead to serviceable formulæ for the interpretation of our experimental data. Nevertheless, by treating pure mass-law effects before dealing with mass-law and ionic-strength effects in combination, the processes at work can be better explained than if we were at this stage to introduce both factors (and their mode of combination, which is not simple) into a single equation, as eventually we shall have to do in order to develop practically useful formulæ.

FIG. 2.

*Solvent Influence on Ionic Strength Effect.*
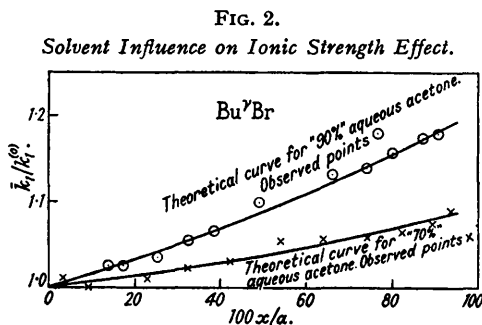


Hydrolysis of *tert.*-butyl bromide in " 90% " and " 70% " aqueous acetone at 25°. (Experimental points, and theoretical curves calculated without disposal constants.)

We set out the mechanism again for convenience, and allow $v_1$, $v_2$, and $v_3$ to represent the instantaneous rates of the corresponding stages, *i.e.*, the numbers of molecules or ions converted per second at any chosen moment :

$$RX \underset{(2)}{\overset{(1)}{\rightleftharpoons}} R^+ + X^- \xrightarrow{(3)} ROH + H^+ + X^-$$
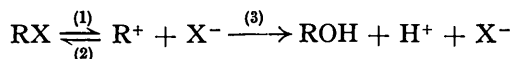
We assume that $v_1$, $v_2$, and $v_3$ are given by the equations

$$v_1 = k_1[RX], \ v_2 = k_2[R^+][X^-] \text{ and } v_3 = k_3[R^+]$$

respectively. The first of these equations is required by the well-known first approximation kinetics of unimolecular hydrolyses. The second and third are indicated, not only by common sense, but by what was found (preceding paper) when we added to the above system another reaction (2′), of the same nature as (2), by introducing an anion $Y^-$ so chosen that RY was completely stable :

$$R^+ + Y^- \xrightarrow{(2')} RY$$
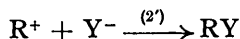
We showed that reaction (2′) was unimolecular with respect to $Y^-$ (azide ions), and that reactions (2′) and (3) had the same molecularity with respect to $R^+$. We assume, as usual, that $k_1$ is much smaller than $k_3$. This means that, throughout the measurable part of the reaction, the amount of material held up in the form $R^+$ is a negligible fraction of the total, so that the numbers of $R^+$ ions formed and destroyed per second can be equated : $v_1 = v_2 + v_3$. The rate which we measure when, for instance, we estimate $[H^+]$ is $v_3$. Using

the last-mentioned equation to eliminate the unknown concentration [R$^+$] from the expression for $v_3$, we have

$$\frac{dx}{dt} = v_3 = \frac{v_1}{v_2 + v_3} \cdot v_3 = \frac{k_1[RX]}{k_2[X^-] + k_3} \cdot k_3 = \frac{k_1(a-x)k_3}{k_2x + k_3} = \frac{k_1(a-x)}{\alpha x + 1} \quad . \quad (5)$$

where we have written $a - x$ for [RX] and $x$ for [X$^-$] in accordance with usual notation.

The constant $\alpha = k_2/k_3$ is the essential measure of the intensity of the mass-law effect. If it is so small that $\alpha x$ is negligible in comparison with unity over the whole range of variation of $x$, in short, if $\alpha a$ is negligible compared with unity, then the reaction will accurately obey the first-order rate law, of which the constant is simply $k_1$, the rate constant of stage (1). If $\alpha a$ is not negligible compared with unity, then there will be deviations in the sense that the specific rate $(dx/dt)/a - x)$ will fall progressively as $x$ increases. However, at the commencement of reaction $(x = 0)$ the specific rate, $k_1^{(0)}$, will again be equal to $k_1$, the rate constant of ionisation (cf. p. 982). Ionic-strength effects, being absent at the commencement of reaction, do not disturb this last identification.

Fig. 3.

Idealised Mass-law Effect.
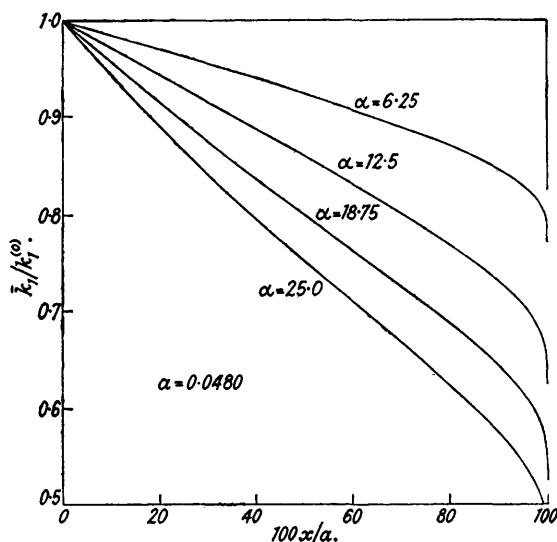


The solution of equation (5) is

$$k_1 = t^{-1}[2 \cdot 303(1 + \alpha a) \log_{10}\{a/(a-x)\} - \alpha x]$$

and, on comparing this equation with equation (4), which defines the integrated first-order rate constants, $\bar{k}_1$, by whose variation we have expressed our observed kinetic deviations, we find that these variable constants are connected to the true constant, $k_1$, by the relation

$$\bar{k}_1 = (k_1 + \alpha x/t)/(1 + \alpha a)$$

Noting that the limit of $x/t$ at $t = 0$ is $k_1 a$, we see that $\bar{k}_1$ will range, as reaction proceeds, from its initial value $k_1^{(0)} = k_1$ to the smaller, final value $k_1/(1 + \alpha a)$, i.e., that $\bar{k}_1/k_1^{(0)}$ will range from 1 to $1/(1 + \alpha a)$. Curves showing the variation of $\bar{k}_1/k_1^{(0)}$ for a particular value of $a$ and several assumed values of $\alpha$ are plotted in Fig. 3. Comparing these descending curves with the ascending curves of Figs. 1 and 2, one supposes that the combination of mass-law and ionic-strength effects must lead to curves lying between the curves appropriate to the separate effects. This is true, although we should go wrong if we were to assume that the curves for the combination of effects would have an intermediate curvature.

(b) *Combination of mass-law and ionic-strength effects.* It is obvious from the preceding sub-section that as soon as we find values of $\bar{k}_1/k_1^{(0)}$ dropping below unity we can be sure, independently of other evidence, that the unimolecular mechanism is under observation. Therefore we may expect to discover certain details concerning this mechanism by investigating the combination of mass-law and ionic strength effects and comparing the results with the observational data.

This combination of the two effects is not straightforward. In the first place they do not combine merely as superposed but independent influences : there is a mutual relation in that the mass-law effect lends to the ionic-strength effect an accelerating power additional to that which the latter would have had in the absence of the former. This arises in the following way.

As shown in Section (1), the ionic-strength effect increases $v_1$ according to the equation

$$v_1 = k_1^{(0)}(a - x)\ \text{antilog}_{10}(0.912 \times 10^{16}\sigma x/D^2 T^2) \quad . \quad . \quad . \quad . \quad (6)$$

where $k_1^{(0)}$ is the rate constant for stage (1) at zero ionic strength, and is equal to the limit to which measured first-order rate constants tend on approaching zero ionic strength. When $v_2$ is negligible in comparison with $v_3$, *i.e.*, when there is no appreciable mass-law effect, this is the sole disturbance to the measured rate. However, when $v_2$ is not negligible compared with $v_3$, *i.e.*, when there is a mass-law effect, then the ionic-strength effect can modify $v_2$ and $v_3$ differently, thereby partially diverting the reaction from route (2) into route (3) ; this also increases the measured rate, because it is in route (3) that the measurement of reaction progress is made.

In order to calculate this diverting action, we must calculate the ionic-strength effect in stages (2) and (3) separately. The effect on stage (2) is easily calculated for great dilution, because we are already convinced (preceding sub-section) that this stage is unimolecular with respect to each of the participating ions, $R^+$ and $X^-$. Therefore it is necessary only to introduce into the right-hand side of our previous equation, $v_2 = k_2[R^+][X^-]$, the Brönsted activity correction, $f_+f_-/f_T$, where $f_T$, the activity coefficient of the transition state, is given by equation (2), whilst, to the approximation to which we are working, $f_+$ and $f_-$, the activity coefficients of the ions, are given by Debye's formula,

$$-\ln f_+ = -\ln f_- = \sqrt{\frac{2}{1000}} \cdot \frac{N^{\frac{1}{2}}e^3}{k^{3/2}} \cdot \frac{\mu^{\frac{1}{2}}}{(DT)^{3/2}} \cdot \quad . \quad . \quad . \quad . \quad (7)$$

We prefer not to strive for greater accuracy by using the second approximation theory of Debye and Hückel, because this would involve the undesirable introduction of a disposable parameter. Inserting the values of the universal constants, and writing $x$ for $[X^-]$, we find

$$v_2 = k_2^{(0)}[R^+]x\ \text{antilog}_{10}\{(0.912 \times 10^{16}\sigma x/D^2 T^2) - (3.63 \times 10^6 x^{\frac{1}{2}}/D^{3/2}T^{3/2})\} . \quad (8)$$

where $k_2^{(0)}$ is the value of $k_2$ at zero ionic strength.

The complication with regard to stage (3) is that, although it must be unimolecular with respect to the ion $R^+$, we have, at the outset, only semi-intuitive reasoning to tell us whether to treat it as unimolecular or multimolecular with respect to water. However, we can try both hypotheses, which are strongly differentiated in their consequences, and decide finally between them after comparison with the results of experiment.

We may first consider " *Hypothesis I,*"—that stage (3) is unimolecular with respect to water. Then the activity coefficient, $f_{+aq}$, of the transition state, $(R \cdots\cdots OH_2)^+$, of stage (3) will closely approximate to $f_+$, the activity coefficient of $R^+$. Since in any single kinetic run the activity of the water is constant, we may regard the factors $[H_2O]f_{H_2O}$ as absorbed in the reaction constant $k_3^{(0)}$. Thus Brönsted's activity correction factor reduces to $f_+/f_{+aq} = 1$, and the rate equation is simply

$$v_3 = k_3^{(0)}[R^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Independently of the results of our experiments, we should have been fundamentally unwilling to believe in this equation for the following reason. Mechanism $S_N1$ for the aqueous hydrolysis of alkyl halides implies a time-lag between stages (1) and (3) : when

the time-lag vanishes, then this mechanism degenerates into the single-stage mechanism $S_N2$. Now the cation $R^+$ formed in mechanism $S_N1$ must be highly energised, and we may suppose that, if it does not already contain the activation energy of stage (3), then it can very easily acquire that energy by collision with surrounding water molecules. Therefore we are disposed to regard, as the main reason for the time-lag, the small statistical probability of the transition state of stage (3). But this implies a complex configuration, considerably more complex, we suppose, than is possible for $(R \cdots \cdots OH_2)^+$.

We know that many water molecules must contribute the solvation energy necessary to secure the splitting of the carbon-halogen bond in stage (1), and that therefore the cation $R^+$ must be formed within an aqueous solvation shell. Hypothesis I treats this cation as ending its life when the shell is pierced by an energised water molecule coming from the external medium. But since all the elements of reactivity are present in the shell itself, it is much more likely that it ends its history by collapse, after having come into a critical phase—its transition state.

In the preceding paper we showed, in the example $R =$ dimethylbenzhydryl, that the relative frequency with which the solvation shell of $R^+$ was pierced by foreign anions, $Y^- = N_3^-$, to produce RY, and, therefore, the relative frequency with which the shell underwent the alternative process of collapse to form ROH, were both independent of the macroscopic water concentration over the investigated five-fold range. Although we should not necessarily postulate such a complete independence for all alkyl cations, the result shows that the composition and constitution of the solvation shell of the dimethyl-benzhydryl cation are essentially independent of the composition of the external medium within the range over which this was varied. It shows, furthermore, that this shell is " water tight " enough effectively to protect the cation from attack by water molecules coming from the external medium. That is another reason why we envisage the shell as collapsing, rather than as being pierced by high-velocity water molecules.

Thus two lines of *a priori* argument, and one deduction from experimental results converge to indicate " *Hypothesis II*," which is that stage (3) is multimolecular with respect to water. We may here anticipate what we have yet to show by claiming the success of this hypothesis in relation to our kinetic measurements as a second experimental confirmation of the same conclusion.

The transition state f(  1e collapse of the shell may be schematically represented $[R \cdots OH \cdots (H \cdots OH \cdots)_n H]^+$ (with $n$ large), and its important feature from the kinetic standpoint is the very large spatial (three-dimensional) distribution of the positive charge. This means that we cannot calculate its activity coefficient by means of Debye's limiting law. As the spatial distribution is increased, the extra factor which enters into the Debye–Hückel law causes $- \ln f_{+aq}$ to approach zero, and, indeed, for our concentrations, zero will be a better approximation than the right hand side of equation (7).* Confining our treatment, as heretofore, to the best approximation that can be made without introducing disposable constants, we see that the Brönsted correction factor becomes $f_+/f_{+aq} = f_+$, with $f_+$ as given by equation (7). Thus the rate equation is

$$v_3 = k_3^{(0)}[R^+]/\text{antilog}_{10}(1.815 \times 10^6 x^{\frac{1}{2}}/D^{3/2}T^{3/2}) \quad . \quad . \quad . \quad . \quad (10)$$

For completeness we also investigate two other conceivable hypotheses. One is *Hypothesis III, viz.*, that under our condition of hydrolysis the alkyl cation is destroyed by the attack of a hydroxide ion. The transition state is now a dipole, whose activity coefficient, $f_{T'}$, will be given by an equation like (2) but with $\sigma'$ written for $\sigma$. The Brönsted factor will be $f_+f_-/f_{T'}$. Since the concentration of hydroxide ions varies inversely as $x$, the rate equation will be

$$v_3 = k_3^{(0)}[R^+]x^{-1} \text{antilog}_{10}\{(0.912 \times 10^{16}\sigma'x/D^2T^2) - (3.63 \times 10^6 x^{\frac{1}{2}}/D^{3/2}T^{3/2})\} \quad . \quad (11)$$

Finally we may consider *Hypothesis IV, viz.*, that under our conditions the cation is destroyed by a hydroxide ion acting in collaboration with many water molecules. The transition state is now the diffuse, neutral mass, $R \cdots OH \cdots (H \cdots OH \cdots)_n$

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* Professor G. B. Kistiakowsky drew our attention to this in the course of a private discussion.

(again $n$ large), and thus its activity coefficient may be set equal to unity. Therefore the rate equation is

$$v_3 = k_3^{(0)}[R^+]/x \text{ antilog}_{10}(3 \cdot 63 \times 10^6 x^{\frac{1}{2}}/D^{3/2}T^{3/2}) \quad . \quad . \quad . \quad . \quad (12)$$

In order to obtain expressions, corresponding to these four hypotheses, for the measured rate $dx/dt$, we substitute in the mass-law equation (5) for $v_1$ by means of equation (6), for $v_2$ by means of equation (8), and for $v_3$ by means of equations (9), (10), (11) and (12), severally. Thus we obtain the following :

*(Hypothesis I)*

$$\frac{dx}{dt} = \frac{k_1^{(0)}(a - x)}{\alpha^{(0)}x \text{ antilog}_{10}(-3 \cdot 63 \times 10^6 x^{\frac{1}{2}}/D^{3/2}T^{3/2}) + \text{antilog}_{10}(-0 \cdot 912 \times 10^{16}\sigma x D^2 T^2)} \cdot \quad (13)$$

*(Hypothesis II)*

$$\frac{dx}{dt} = \frac{k_1^{(0)}(a - x)}{\alpha^{(0)}x \text{ antilog}_{10}(-1 \cdot 815 \times 10^6 x^{\frac{1}{2}}/D^{3/2}T^{3/2}) + \text{antilog}_{10}(-0 \cdot 912 \times 10^{16}\sigma x/D^2 T^2)} \quad (14)$$

*(Hypothesis III)*

$$\frac{dx}{dt} = \frac{k_1^{(0)}(a - x)}{\alpha^{(0)}x^2 \text{ antilog}_{10}(-0 \cdot 912 \times 10^{16}\sigma' x/D^2 T^2) + \text{antilog}_{10}(-0 \cdot 912 \times 10^{16}\sigma x/D^2 T^2)} \quad (15)$$

*(Hypothesis IV)*

$$\frac{dx}{dt} = \frac{k_1^{(0)}(a - x)}{\alpha^{(0)}x^2 + \text{antilog}_{10}(-0 \cdot 912 \times 10^{16}\sigma x/D^2 T^2)} \quad . \quad . \quad . \quad . \quad (16)$$

(c) *Applications to experimental data.* The last four equations all contain $\alpha^{(0)} = k_2^{(0)}/k_3^{(0)}$, the characteristic constant expressing the strength of the mass-law effect. We shall treat $\alpha^{(0)}$ in this section as a disposable constant, although in Section (5) we shall find that it is capable of being independently determined through the effect of added salts. All four equations also contain $\sigma$, the characteristic constant for the ionic-strength effect in processes (1) and (2) of mechanism $S_N'$. As we do not want to have to adjust two parameters, we shall take advantage of the circumstance that $\sigma$ can be found simply and independently from salt effects, as is shown in Section 4. Equation (15) contains also $\sigma'$, the constant which characterises the ionic-strength effect in process (3) according to Hypothesis III. This constant cannot be very different from the known constant $\sigma$, and in applying equation (15) we shall assume that $\sigma' = \sigma$, as no tenable assumption about $\sigma'$ makes any difference to the conclusion we shall reach, *viz.*, that equation (15) is wrong anyhow.

The most sensitive kinetic experiment we have with which to test these formulæ is the hydrolysis of 0·0463M-dimethylbenzhydryl chloride in " 90% " aqueous acetone at 0° (preceding paper) : both the mass-law and the ionic-strength effect are here particularly powerful, because $\alpha^{(0)}$ and $\sigma$ are each greater than for any other of the investigated halides, and because the solvent has a small water content; also the kinetics in this solvent are rather accurately measured, as the rate is of a convenient order. Using the appropriate values of $D$ and $T$, and the value $10^8\sigma = 2 \cdot 73$ determined in Section (4), we combine, in turn, the numerically integrated form of each of the equations (13)—(16) with equation (4), eliminate $t$, and thus calculate what should, according to each of the four hypotheses, be the dependence of $\bar{k}_1/k_1^{(0)}$, the proportional change in the integrated, first-order rate constant, on $100x/a$, the percentage progress of reaction; and in the case of each hypothesis we do this for various assumed values of the mass-law constant, $\alpha^{(0)}$, seeking that value which gives the best agreement with experiment.

The results are illustrated in Fig. 4. For Hypotheses I, III, and IV there is no value of $\alpha^{(0)}$ which will lead to agreement with experiment : the curves for Hypothesis I pass through a minimum, whilst those for Hypotheses III and IV have maxima and are concave to the origin. We show but one curve for each of these hypotheses, the parameter, $\alpha^{(0)}$, being in each case chosen to give about the right integrated rate constant at 60% of reaction. Hypothesis II alone yields curves of the correct general form, *viz.*, curves which

fall steadily and are convex to the origin. The curve for $\alpha^{(0)} = 69$ agrees with the experimental data to within the limits of accuracy of the latter. Two other curves of the same family, but with different values of $\alpha^{(0)}$, are also plotted in order to give an indication of the dependence of the slope on $\alpha^{(0)}$.

The above comparison indicates Hypothesis II to the exclusion of its alternatives, and almost any of our experiments on the kinetics of hydrolysis of simple and substituted benzhydryl halides could have been used to similar effect. As anyone interested will be able to verify this statement by calculation from the data and formulæ given, we shall not pursue further illustrations of the comparative merits of the four hypotheses, but will henceforth take it for granted that no further discussion of Hypotheses I, III, and IV is necessary.*

The interpretation expressed by the curve labelled " II, $\alpha^{(0)} = 69$ " represents a specified, accelerating ionic-strength effect, and a specified retarding mass-law effect, combined in a particular way. Some check on this interpretation can be obtained by passing to more

FIG. 4.

*Kinetics of Hydrolysis of 0·0463м-pp'-Dimethylbenzhydryl Chloride in " 90% " Aqueous Acetone at 0°.*
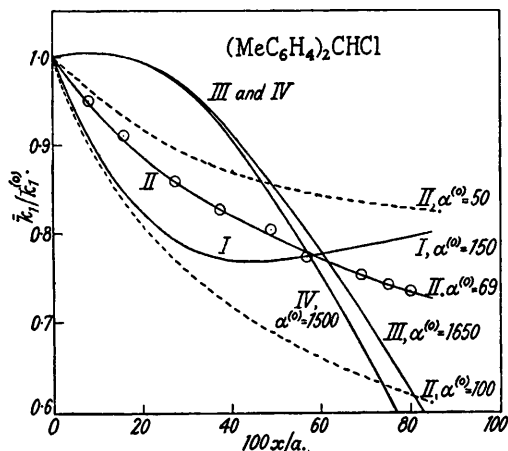


I, II, III, IV = theoretical curves according to Hypotheses I, II, III, IV respectively [$10^8\sigma = 2\cdot73$, $\alpha^{(0)}$ as shown]. ⊙ = experimental observations (this vol., p. 974).

aqueous solvents; for then the ionic-strength effect will be cut down by calculable amounts, the mass-law effect will remain essentially the same, and the mode of combination will have been determined. The first of these statements can be accepted because the ionic-strength effect depends on the solvent through its macroscopic dielectric constant only; the second follows because we have already shown, by means of experiments with azide ions, that the properties of the hydration shell through which anions attack the alkyl cation are independent of the solvent for our range of solvents. Thus everything is determinate : we must use equation (14) with $\alpha^{(0)} = 69$, $10^8\sigma = 2\cdot73$, and the appropriate $D$ and $T$. This test has been carried out in relation to our kinetic experiments in " 85% " and " 80% " aqueous acetone, and the agreement is good, although, owing to the rapidity of hydrolysis in these solvents, the experimental results are not highly accurate and the points representing observations show considerable scatter about the theoretical curves. In order to illustrate the solvent effect the theoretical curves, and the corresponding observations, for " 90% " and " 80% " aqueous acetone are compared in Fig. 5; the results for " 85% " aqueous acetone fall, as they should, about a curve lying between those shown.

* It will be appreciated that it is only for hydrolysis in neutral and in acidic solutions that we have as yet proved that Stage 3 has only one mechanism, *viz.*, that of Hypothesis II. We hope in due course to ascertain whether or not large concentrations of hydroxide ions bring about an incursion of some other mechanism of alkyl cation hydroxylation; the most probable one is that represented by Hypothesis IV.

FIG. 5.

*Solvent Effect on Kinetics of Hydrolysis of* pp′-*Dimethylbenzhydryl Chloride in Aqueous Acetone at* 0°.
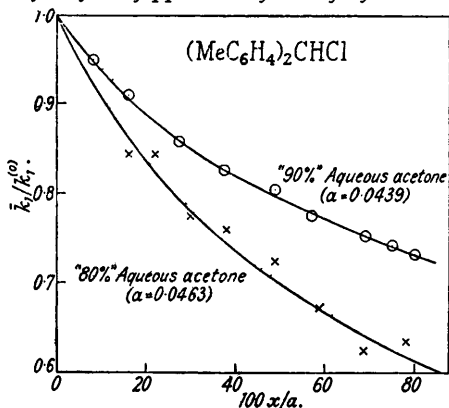


[Observations, ⊙ for " 90% " aqueous acetone and × for " 80% " aqueous acetone, are compared with the curves required by the time-eliminant of equations (4) and (14). The upper curve determines the disposable constant, $a^{(0)} = 69$, which then fixes the lower curve. The values, $a$, refer to the initial concentration of the alkyl halide, which enters into the theoretical formula.]

FIG. 6.

*Kinetics of Hydrolysis of some Further Alkyl Chlorides in Aqueous Acetone.*
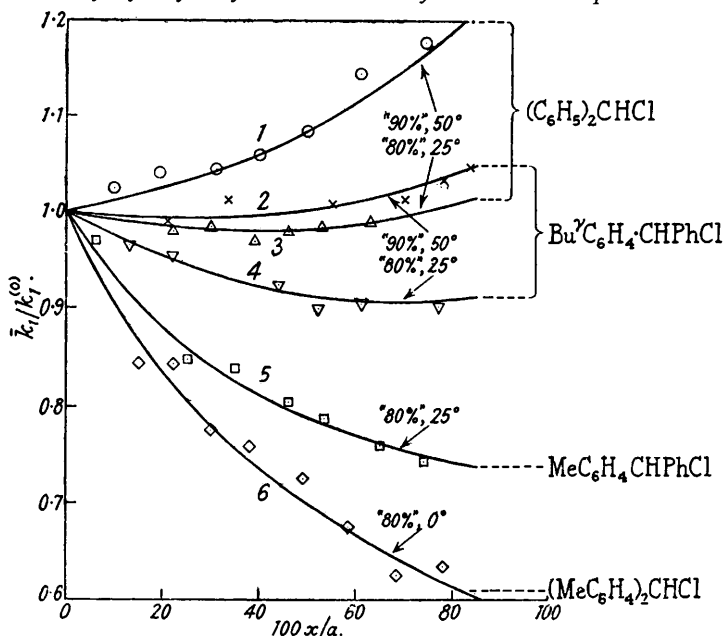


Curves of Eliminant of Equations 4 and 14.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Curve 1. | $a^{(0)} = 10$; | $10^8 \sigma = 1.62$; | " 90% " aq. acetone; | 50·0°; | $a = 0.0968$. |
| ,, 2. | ,, 20; | ,, 2.22; | " 90% " ,, | ,, ; | ,, 0.0471. |
| ,, 3. | ,, 10; | ,, 1.62; | " 80% " ,, | 25·0°; | ,, 0.1015. |
| ,, 4. | ,, 20; | ,, 2.22; | ,, ,, | ,, ; | ,, 0.0794. |
| ,, 5. | ,, 35; | ,, 2.22; | ,, ,, | ,, ; | ,, 0.1005. |
| ,, 6. | ,, 69; | ,, 2.73; | ,, ,, | 0·0°; | ,, 0.0463. |

Observations.

| | | |
|---|---|---|
| ⊙ Benzhydryl chloride | ................................ | solvent, temperature, and initial concn. as for Curve 1. |
| × *p-tert.*-Butylbenzhydryl chloride | ............ | ,,    ,,    ,,    ,,    ,,    ,,    2. |
| △ Benzhydryl chloride | ................................ | ,,    ,,    ,,    ,,    ,,    ,,    3. |
| ▽ *p-tert.*-Butylbenzhydryl chloride | ............ | ,,    ,,    ,,    ,,    ,,    ,,    4. |
| ⊡ *p*-Methylbenzhydryl chloride | ............... | ,,    ,,    ,,    ,,    ,,    ,,    5. |
| ◇ *pp′*-Dimethylbenzhydryl chloride | ............ | ,,    ,,    ,,    ,,    ,,    ,,    6. |

Having now discussed in detail the kinetics of the hydrolysis of our two extreme examples, *tert.*-butyl bromide and *pp'*-dimethylbenzhydryl chloride, it remains to be shown that the intermediate members of the alkyl halide series also exhibit kinetics represented by equation (14). According to the position of the alkyl group in the series, *i.e.*, according to the length of time that the solvation shell of the alkyl cation normally survives before internal collapse, the various alkyl halides will have mass-law constants, $\alpha^{(0)} = k_2^{(0)}/k_3^{(0)}$ (representing the efficacy with which these solvated cations are destroyed by their own anions) which range from some small value, supposed on indirect reasoning to be of the order 1—2 for *tert.*-butyl bromide, to 69, the value for *pp'*-dimethylbenzhydryl chloride. From the point of view of the alkyl series, we should consider the alkyl chlorides and alkyl bromides separately, because the reactivity of the bromide ion towards a particular alkyl cation is considerably greater than that of the chloride ion. We find for benzhydryl chloride the value 10, for *p-tert.*-butylbenzhydryl chloride 20, and for *p*-methylbenzhydryl chloride 35; benzhydryl bromide has the larger value 50. With these constants, and the values determined in Section 4 for the ionic-strength constants, $\sigma$, together with the experimental temperature, the dielectric constant of the solvent used, and the initial concentration of alkyl halide taken, we can, for each kinetic experiment, construct the curves defined by the time-eliminant of equations (4) and (14). We find that in all cases these curves express the observations to within the limits of accuracy of the latter. The solvent influence is accounted for, even for those halides in which the ionic-strength and the mass-law effect are so nearly balanced that the qualitative behaviour of the specific rate (its rise, fall, or approximate constancy) can be changed by changing the solvent. The comparison of theory and practice for as many of these experiments as can be represented without confusion on a single diagram is shown in Fig 6.

By reference to Table I (p. 981) the reader will be reminded that the progressive retardations of the specific rate illustrated in Figs. 4, 5, and 6 are impossible on the single-stage, bimolecular mechanism of hydrolysis.

### (4—5) *Influence of Added Salts (Method 5).*

(4) *The Ionic-strength Effect as Sole Contributor to the Salt Influence.*—(a) *Theory.* Reference to Table I will indicate the circumstances in which we might expect only the ionic-strength effect to contribute to the salt influence. Three cases arise. Considering first the unimolecular mechanism, we expect to observe a substantially pure ionic-strength effect when ionised salts are added in the hydrolysis of a halide, such as *tert.*-butyl bromide, which shows a nearly pure ionic-strength effect in its hydrolysis without added salts. Independently of whether the anion of the salt is identical with or different from the anion given by the alkyl halide, added salts should accelerate hydrolysis to an extent which can be calculated if the constant, $\sigma$, characterising the ionic-strength effect is known; or, alternatively, the observed accelerations may be used to determine $\sigma$ independently. With either method of treatment, the solvent influence on the acceleration can be predicted. Concerning the bimolecular mechanism, all that we can say in relation to this particular application is that the ionic-strength acceleration should be much smaller than would be calculated by the methods considered—and therefore much smaller than the acceleration found, since we shall show that this agrees quite well with the calculations.

The next case relates to halides, such as the simple and substituted benzhydryl halides which show a marked mass-law effect in their hydrolysis without added salts. In the unimolecular mechanism, the mass-law effect of salts whose anions are identical with that of the alkyl halides should contribute a retarding influence. In the bimolecular mechanism, however, the mass-law effect does not enter with salts of this type, and we are left simply with the small ionic-strength acceleration. As in our experiments on all simple and substituted benzhydryl halides with added salts of the " common-ion " type we observe retardations, it is obvious that, once again, the bimolecular mechanism cannot be accommodated to the observations. Therefore we need only discuss the unimolecular mechanism, and, in relation to this class of example, the discussion is best reserved for Section 5, where we shall be dealing with superposed ionic-strength and mass-law effects.

The third case relates to the same series of alkyl halides and to added salts whose anions

are different from those of the alkyl halides. In this case, according to the unimolecular mechanism, the mass-law effect does not arise in the *initial* part of reaction, and we are left with a pure ionic-strength effect, which should be covered by the theory already illustrated. As before, the solvent-dependence of this effect can be calculated. During the later stages of reaction we shall have a mass-law effect arising from the anions liberated in hydrolysis from the alkyl halide itself; the discussion of this phenomenon, and of the manner in which it is modified by the added salt, is reserved for Section 5. The bimolecular mechanism requires a mass-law effect (attack by the added anions on alkyl halide molecules), but the resulting acceleration should agree with the composition of the reaction product, if the latter is stable. Though proof is deferred to Section (5), we may state here that there is, on the contrary, a marked disagreement between rate and composition. These considerations enable us to reduce the contents of this Section essentially to a discussion of the first and third of the three cases, each in relation to the unimolecular mechanism only. The quantitative theory is implicit in the formulæ already given in Section 2.

(b) *Application to experimental data :* tert.-butyl bromide. In the case of *tert.*-butyl bromide,* we have already obtained the ionic-strength parameter $10^8\sigma = 0.74$ from the kinetics in the absence of salts, and have confirmed its correct order of magnitude by means of a rough calculation based on the Morse function. From this value of $\sigma$ we can at once calculate by what factor the initial rate should be increased by the addition of any fully ionised, uni-univalent electrolyte of concentration $c$. The formula, which follows from equation (3), is,

$$k_1^{(c)}/k_1^{(0)} = \text{antilog}_{10}(0.912 \times 10_{16}\sigma c/D^2 T^2) \quad . \quad . \quad . \quad . \quad (17)$$

Comparing the calculated values with those given by the experiments already recorded, we obtain the figures in Table III, columns 4 and 5. The agreement is good, considering the approximations in the theory and the difficulty of achieving a precision better than, say, 2%, in the measurements. We do not know whether it is significant that the observed accelerations are all very slightly higher than the calculated, but if we accept the observed figures and then calculate the values of $10^8\sigma$ required to give exact agreement, we obtain the figures of column 6, which are naturally a little higher than the value, 0·74, already deduced ($\sigma$ is rather sensitive to small changes in the $k$-ratio).

TABLE III.

*Effects of Added Salts on the Initial Rate* ($k_1$ *in sec.*$^{-1}$) *of Hydrolysis of* tert.-*Butyl Bromide in " 90% " Aqueous Acetone at 50·0°.*

| Salt. | $c$. | $10^5 k_1^{(c)}$. | $k_1^{(c)}/k_1^{(0)}$ (found). | $k_1^{(c)}/k_1^{(0)}$ (calc.). | $10^8\sigma$ (calc.). |
|---|---|---|---|---|---|
| None ..................... | 0·0000 | 19·0 | (1·00) | — | — |
| LiBr ..................... | 0·1065 | 27·5 | 1·44 | 1·39 | 0·82 |
| LiCl ..................... | 0·1005 | 26·3 | 1·39 | 1·37 | 0·78 |
| NaN₃ ..................... | 0·1000 | 26·5 | 1·40 | 1·36 | 0·80 |

We can use these constants in association with the simple extension, (18), of equation (3) in order to calculate the kinetic forms of the reactions occurring in the presence of the added salts :

$$dx/dt = k_1^{(0)}(a - x) \, \text{antilog}_{10}\{0.912 \times 10^{16}\sigma(c + x)/D^2 T^2\} \quad . \quad . \quad . \quad (18)$$

We have to eliminate $t$ between equations (4) and (18), after numerical integration of the latter, thus obtaining, as a function of the percentage progress of reaction in the presence of the salt, the integrated first-order rate constant, reckoned, however, as a multiple of the initial specific rate in the absence of the salt. The results of this type of calculation, as applied to our data for *tert.*-butyl bromide, are not good, as will be seen from the illustration in Fig. 7; and, as we can get much better results in analogous calculations referring to experiments at higher dilution (p. 996), we take this to mean that our formulæ, which really

* For the reason given in the footnote on p. 984, the circumstance that a small part of the measured reaction of *tert.*-butyl bromide consists in the formation of *iso*butylene does not affect our argument here, in relation either to the initial rates, or to the kinetic form of hydrolysis, in the presence of added salts.

belong to the region of very dilute solution, give a good account of experiments in which the ionic strength, $\mu$, is less than a certain limit (0·04—0·10, depending on the alkyl halide), but fail appreciably when applied to experiments in which the ionic strength rises from 0·1 to 0·2. It can be shown that the deviation is in the expected direction (p. 996).

(c) *Application to experimental data : Simple and substituted benzhydryl halides and "non-common ion" salts.* By "non-common ion" salts we mean salts whose anions are not the same as the anion given by the alkyl halide. In these examples, in which a pure ionic-strength effect is to be expected in the initial stages of reaction, we find ourselves without any independent means of measuring the characteristic constant $\sigma$, and have no recourse but to employ the observed initial accelerations produced by the added salts for the determination of this constant. We can, however, obtain some check by changing the conditions, the two most important conditions being the solvent and the concentration of added salt : from the observed acceleration of initial rate, $k_1^{(c)}/k_1^{(0)}$, for one particular solvent-composition, temperature and salt-concentration, the acceleration for other values of these variables can be calculated by eliminating $\sigma$ between two equations of form (17), containing the appropriate values of $D$, $T$, and $c$. The results of some calculations of this type are compared with the results of observations in Table IV. The agreement is in all

FIG. 7.

*Kinetics of Hydrolyses of* 0·1056M-*tert.-Butyl Bromide in the Presence of* 0·1065M-*Lithium Bromide in* "90%" *Aqueous Acetone at* 50·0°.
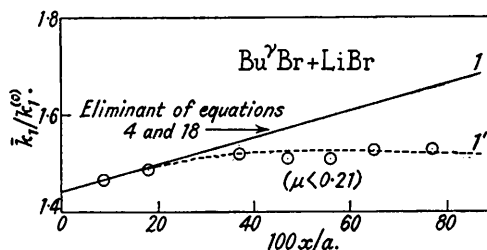


[*Curve* 1 : ($\mu$, 0·1065 → 0·2121) $10^8\sigma = 0·82$. Curve 1′ : experimental deviation from Curve 1.

cases good. The first three relate essentially to solvent changes, and the fourth to a concentration change. The last is a particularly simple confirmation of the conclusion that the ionic-strength effect depends on an exponential function of the *first* power of the ionic strength ($e^{\text{const.}\cdot\mu}$), as it should from the theory of dipole-ion interaction, and neither on the less steeply ascending square-root function ($e^{\text{const.}\cdot\sqrt{\mu}}$) of the Debye theory of ion-ion interaction, nor on any such more steeply ascending function as would almost certainly have been required if the transition state of the rate-controlling process had been of such form that we ought to have treated it as a multipole.*

TABLE IV.

*Effect of Conditions on the Acceleration, produced by Sodium Azide, of the Initial Reaction Rate of Alkyl Halides in Aqueous Acetone.*

| Alkyl halide. | Conditions for which $k_1^{(c)}/k_1^{(0)}$ is to be given. | | | Given $k_1^{(c)}/k_1^{(0)}$. | Conditions for which $k_1^{(c)}/k_1^{(0)}$ is to be calculated. | | | Calc. $k_1^{(c)}/k_1^{(0)}$. | Found $k_1^{(c)}/k_1^{(0)}$. |
|---|---|---|---|---|---|---|---|---|---|
| | Solv. | Temp. | $c$. | | Solv. | Temp. | $c$. | | |
| Ph$_2$CHCl ............ | "90%" | 50° | 0·1009 | 2·13 | "70%" | 25° | 0·0999 | 1·33 | 1·31 |
| (Me·C$_6$H$_4$)$_2$CHCl ... | ,, | 0 | 0·0512 | 1·71 | "85%" | 0 | 0·0512 | 1·53 | 1·50 |
| ,, | ,, | ,, | ,, | ,, | "80%" | ,, | 0·0540 | 1·40 | 1·40 |
| Bu$\gamma$·C$_6$H$_4$·CHPhCl | ,, | 50 | 0·0501 | 1·70 | "90%" | 50 | 0·1000 | 2·88 | 2·88 |

* In the next paper but one an ionic-strength effect involving the same dependence on salt concentration is established for a halogen-exchange reaction of a benzhydryl halide (F⁻ + RCl ⟶ RF + Cl⁻) in sulphur dioxide solution. This reaction also exhibits strikingly the mass-law effect which diagnoses the unimolecular mechanism that requires the particular form of ionic-strength effect illustrated.

The only other possible check arises from the consideration that in very dilute solution the sole property of the added salt which is of significance in a pure ionic-strength effect is the valency of its ions. As the four salts we have used are all uni-univalent, this means that for any one alkyl halide, and for the same solvent, temperature and (low) salt-concentration, the proportional rate increase $k_1^{(c)}/k_1^{(0)}$ should be independent of which salt is employed. The different salts have not been used in exactly the same concentration, but the concentrations always approximated more or less closely to either 0·05 or 0·1M, and we can easily correct the proportional rate increases, by means of the $e^{\text{const.}\cdot\mu}$-law, to correspond exactly to whichever of these two standard concentrations the actual experimental concentrations were closer to. These corrections are applied in columns 8 and 9 of Table V, in which the values for *tert.*-butyl bromide are included for completeness. The figures bracketed together in these two columns are those which should be identical if the concentration at which comparison is made were small enough. The agreement is good at the lower of the two concentrations, but uneven at the higher one. This is not unexpected, because the correction factors required to give us an accurate law for higher concentrations differ with each salt. Furthermore, since the factor essentially responsible for limiting the validity of our dilute solution law is molecular size, it might have been anticipated that the law would be found applicable up to a higher concentration for the reactions of *tert.*-butyl bromide than for those of any of the benzhydryl halides. The bracketed figures show this; and the same point is illustrated in several other ways later in this paper. Only experiments with " non-common ion salts " are included in the Table, because, in general, " common-ion salts " give very different values owing to the incursion of the mass-law effects.

TABLE V.

*Effect of " Non-common-ion Salts " on the Initial Rate of Reaction of Alkyl Halides in Aqueous Acetone, and Values of the Ionic-strength Constant.*

| Alkyl halide. | Salt. | Solv. | Temp. | c. | $10^5 k_1^{(c)}$. | $k_1^{(c)}/k_1^{(0)}$. | $c=0\cdot05$. | $c=0\cdot1$. | $10^8\sigma$. |
|---|---|---|---|---|---|---|---|---|---|
| Bu$^\gamma$Br | None | " 90% " | 50° | 0·0000 | 19·0 | — | — | — | |
| ,, | LiCl | ,, | ,, | 0·1005 | 26·3 | 1·39 | — | {1·39} | 0·79 |
| ,, | NaN₃ | ,, | ,, | 0·1000 | 26·5 | 1·40 | — | {1·40} | |
| Ph₂CHCl | None | ,, | ,, | 0·0000 | 5·80 | — | — | — | |
| ,, | LiBr | ,, | ,, | 0·0964 | 10·0 | 1·72 | — | {1·76} | 1·61 |
| ,, | NaN₃ | ,, | ,, | 0·1009 | 12·4 | 2·13 | — | {2·12} | |
| ,, | None | " 70% " | 25 | 0·0000 | 32·0 | — | — | — | |
| ,, | NaN₃ | ,, | ,, | 0·0999 | 41·8 | 1·31 | — | 1·31 | |
| Ph₂CHBr | None | " 90% " | 50 | 0·0000 | 201 | — | — | — | 1·74 |
| ,, | NaN₃ | ,, | ,, | 0·1007 | 416 | 2·07 | — | 2·06 | |
| Bu$^\gamma$·C₆H₄·CHPhCl | None | ,, | ,, | 0·0000 | 55·0 | — | — | — | |
| ,, | LiBr | ,, | ,, | 0·1035 | 107 | 1·95 | — | {1·91} | 2·22* |
| ,, | NaN₃ | ,, | ,, | 0·1000 | 158 | 2·88 | — | {2·88} | |
| ,, | ,, | ,, | ,, | 0·0501 | 93 | 1·70 | 1·70 | — | |
| (Me·C₆H₄)₂CHCl | None | ,, | 0 | 0·0000 | 9·10 | — | — | — | |
| ,, | NaN₃ | ,, | ,, | 0·0512 | 15·5 | 1·71 | 1·69 | — | |
| ,, | None | " 85% " | ,, | 0·0000 | 47·0 | — | — | — | |
| ,, | LiBr | ,, | ,, | 0·0504 | 68·5 | 1·46 | {1·46} | — | |
| ,, | NaN₃ | ,, | ,, | 0·0512 | 70·5 | 1·50 | {1·48} | — | 2·73 |
| ,, | NMe₄NO₃ | ,, | ,, | 0·0506 | 72·0 | 1·53 | {1·52} | — | |
| ,, | None | " 80% " | ,, | 0·0000 | 160 | — | — | — | |
| ,, | NaN₃ | ,, | ,, | 0·0540 | 224 | 1·40 | 1·37 | — | |

* This approximate value was also adopted for *p*-Me·C₆H₄·CHPhCl in the calculations of Section 3.

(d) *The ionic-strength constant*, $\sigma$. The last column of Table V records the values of $10^8\sigma$, which can be calculated from the data by application of equation (17). We may consider the order of magnitude of these values. It will be recalled that, according to our model in which the transition state is treated as a simple dipole, $\sigma$ has the constitution $z^2 d$, where $z$ is the fraction of the ionic charge which is transferred from carbon to halogen in the transition state of ionisation, and $d$ is the distance between the charges. We neglect the numerical factor which in Kirkwood's investigation varied with the shape of the structure containing the dipole, because in no real case can it be computed, nor can it differ

from unity sufficiently to be important for an order-of-magnitude calculation. We note in the first place that all the $\sigma$-values are of the order 1—2 A., which is correct. Taking $z = \frac{1}{2}$ as a rough approximation, using the Morse relation, and assuming that in the transition state of *tert.*-butyl bromide the whole of the positive charge is located on the tertiary carbon atom, we previously calculated for this substance $10^8\sigma = 0.65$, which agrees sufficiently with the observed value. The much greater observed values for the simple and substituted benzhydryl halides may be attributed, in part at least, to the mesomerism of the transition states of these structures : this tends to locate the positive charge within the benzene rings. On carrying out a similar rough calculation for benzyl chloride and benzyl bromide, with the assumption that $z = \frac{1}{2}$ and that the positive charges are located at the centres of the benzene rings,* we found $10^8\sigma = 1.28$ for the chloride and $1.36$ for the bromide. The small difference between the two halides is due essentially to the different sizes of the two halogens, and a similar difference appears in the observed values for benzhydryl chloride and bromide, although these observed figures are greater. The further increase of $\sigma$ with $p$-alkyl substitution is in qualitative agreement with the theory of electron release from these $p$-substituents and especially from $p$-methyl groups (p. 982) : this tends to seat the positive charges still further from the halogen atom in the transition state. It would also be reasonable to suppose that the value of $z$ tends to increase in these aromatic structures, *i.e.*, that, as the electrical capacity of the aralphyl system is increased, a greater charge-transfer becomes necessary in order to determine the eventual fission of the carbon-halogen bond.†

(5) *Ionic-strength and Mass-law Effects as Joint Contributors to the Salt Influence.*— (a) *Theory.* As will be seen from Table I (p. 981), the addition of " common-ion salts," *i.e.*, salts whose anions are identical with the anion given by the alkyl halide, introduces a mass-law effect according to the unimolecular mechanism; and this mass-law effect contributes a retardation of the reaction rate, which may or may not outweigh the normal ionic-strength acceleration. According to the bimolecular mechanism " common-ion salts " should have no mass-law effect, so that this mechanism cannot accommodate an observed retardation of the reaction rate. Since for all but one of the investigated alkyl halides we observe retardations by added " common-ion salts," there is no hope of fitting the bimolecular mechanism to our results in this field, and therefore we shall further consider them only in relation to the unimolecular mechanism.

With added " non-common-ion " salts the position is partly reversed. According to the unimolecular mechanism, such salts contribute no mass-law effect of their own, although after the initial stages of reaction, they will modify the mass-law effect of the anions produced from the alkyl halide itself. The mass-law effect is absent initially because, in the unimolecular mechanism, intervention by added anions occurs only after the rate-deter-

* We assumed also that the activation energy was 23 kg.-cals./g.-mol. in each case, and that the $\overset{\frown}{C-C}$-Hal angle would be close to 180° in the transition state, although it is considerably smaller in the normal state.

† On looking over our previous results in order to discover why we did not detect the deviations from first-order kinetics before 1937, we found the reason to be that almost all the work was done with *tert.*-butyl halides for which the ionic-strength constant is rather small and the mass-law constant very small : even the ionic-strength effect could scarcely have been observed with these halides because of the relatively low initial concentrations and the unfavourable solvent compositions employed. On the other hand, attention was drawn in published experiments on α-phenylethyl chloride to deviations from first-order kinetics, which can now clearly be recognised as an ionic-strength effect (Hughes, Ingold, and Scott, J., 1937, 1201). This is a halide whose position, as judged from its absolute hydrolysis rate, in the series, given on p. 982, would be almost identical with that of *tert.*-butyl chloride, so that we should expect a negligible mass-law effect. On the other hand, owing to the phenyl substituent, we should expect a relatively large ionic-strength effect in accordance with the argument given above. Actually, with the halide initially in 0·16M-concentration in " 80% " aqueous acetone at 70°, the integrated first-order rate constant rose steadily from $8.56 \times 10^{-5}$ sec.$^{-1}$ at 14% of reaction to $9.73 \times 10^{-5}$ sec.$^{-1}$ at 83% of reaction, and a similarly rising constant was obtained by polarimetric observation on the optically active compound. In " 60% " aqueous alcohol, however, in which theory shows that the effect should be greatly reduced, the observed drift was much smaller and occasioned no special remark.

mining stage, and if the anions are " non-common-ions " they do not reverse the rate-determining stage. On the other hand, according to the bimolecular mechanism there is only one reaction-stage, and thus " non-common-ion " salts should contribute a mass-law acceleration, which can be recognised by means of its connexion with the composition of the reaction product. It can be arranged that attack by the added anion shall lead to a stable substitution product, of which the amount formed can be directly estimated : we then know that, in the bimolecular mechanism, its formation must make an additive contribution to the total, measured rate.

We shall examine this last point first, because it is very simple and the results will relieve us of any necessity to consider the bimolecular mechanism further. We shall then trace in more detail the consequences of the unimolecular mechanism. For quantitative purposes we shall combine the ionic-strength and the mass-law effect in accordance with " Hypothesis II " (that hydroxylation of the alkyl cation is multimolecular with respect to water). It is not necessary to develop the requisite formulæ in this sub-section : they follow so directly from the theory of Section 3 that they can be written down from inspection as needed.

(b) *Attempted correlation of reaction rates and product compositions.* The product compositions can be determined when the added salt is sodium azide, because alkyl azides are not hydrolysed under the conditions used. According to the unimolecular mechanism there should be no connexion between the reaction rates and product compositions, because these quantities are determined in different reaction stages. The bimolecular mechanism, however, requires the additive connexion already mentioned. Since the attempted correlation is thus a test for the bimolecular mechanism, in which the ionic-strength effects should be weak, we neglect the latter—especially as it could make no difference to the outcome were we to take them into account. On this basis, we compare in Table VI the proportions in which alkyl azides have been observed to be formed in the initial stages of the reactions of alkyl halides with aqueous acetone in the presence of added sodium azide, with the proportions in which they should have been formed in order to make the correct (bimolecular) contribution to the initial rate. We use initial rates because they have a definite and not a drifting value, and can be correlated with a definite and not a diminishing concentration of azide ions. It will be seen from the Table that in one case this calculated proportion of alkyl azide is much too high, in another it is about right, and in three others it is much too low. Obviously the simple relationship required by the bimolecular mechanism does not obtain.

TABLE VI.

*Observed Product Compositions and Compositions calculated on the Bimolecular Mechanism for Reactions of Alkyl Halides with Aqueous Acetone containing Sodium Azide.*

| | Conditions. | | | | Initial proportion $RN_3$. | |
| --- | --- | --- | --- | --- | --- | --- |
| Alkyl halide. | Solvent. | Temp. | *c.* | $k_1^{(c)}/k_1^{(0)}$. | Obs. (%). | Calc. (%). |
| $Bu^\gamma Br$ ..................... | " 90% " | 50° | 0·1000 | 1·40 | 5 | 28·5 |
| $Bu^\gamma \cdot C_6H_4 \cdot CHPhCl$ ...... | ,, | ,, | 0·0501 | 1·70 | 40 | 41·2 |
| $(Me \cdot C_6H_4)_2 CHCl$ ......... | ,, | 0 | 0·0512 | 1·71 | 67 | 41·5 |
| ,,         ......... | " 85% " | ,, | 0·0512 | 1·50 | 66 | 33·3 |
| ,,         ......... | " 80% " | ,, | 0·0540 | 1·40 | 66 | 28·5 |

(c) *Internal comparison of product compositions.* Experiments with added salts whose intervention leads to a stable substitution product can be made the basis of another simple test of mechanism—a test in which the positions of the unimolecular and the bimolecular mechanism are reversed, since it is now the former that supplies the relationship to be looked for. If we carry out parallel reactions with two alkyl halides containing the same alkyl group, say, an alkyl chloride and the corresponding alkyl bromide, each in the presence of the same added salt in the same concentration, then, according to the bimolecular mechanism, no particular relation should exist between the compositions of the products obtained in the two experiments, because the added anion is attacking different entities, the alkyl chloride and the alkyl bromide molecules. On the other hand, the unimolecular mechanism involves the definite requirement that the compositions of the two products

should be identical, because in this mechanism the added anion attacks the alkyl cation, which is the same for both alkyl halides. This, then, is essentially a test for the unimolecular mechanism. The necessary comparison of product compositions is available in the reactions of benzhydryl chloride and benzhydryl bromide in aqueous acetone containing sodium azide. The rates of these reactions are very different, but, as is shown in Table VII, the product compositions are identical to within the limits of precision of the measurements; that is to say, the requirement of the unimolecular mechanism is satisfied. It should be explained that we are here comparing the product-compositions, not, as before, for the initial stages of reaction, but for the nearly completed reactions. We are allowed to do this, because, although different halide ions are liberated in the two hydrolyses, their attack does not affect the competition between azide ions and water, but only restores some original alkyl halide molecules, which will later ionise again to regenerate the alkyl cation that sooner or later must inevitably be partitioned between the azide ions and water; and we prefer to use the nearly completed reaction because the accuracy of the determined compositions is greater : initial product compositions, being based on dynamical measurements, are subject to an error of more than 2%, whereas the compared compositions are accurate to less than 1%; if we could delay analysis until all reaction had completely ceased, the accuracy would be higher still (0·2%), but this procedure is precluded by the slight reversibility of the hydrolyses, which, though it could not be measured under the conditions of these experiments, must be taken into account as a possible source of disturbance to the compositions at infinite time.

TABLE VII.

*Comparison of Product Compositions for Reactions of Alkyl Halides having the same Alkyl Radical with Aqueous Acetone containing Sodium Azide.*

| Halide. | Solvent. | Temp. | $c$. | $10^5 k_1^{(c)}$. | ROH (%). | $RN_3$ (%). |
|---|---|---|---|---|---|---|
| Ph₂CHCl .................. | " 90% " | 50° | 0·1009 | 12·4 | 66·0 | 34·0 |
| Ph₂CHBr ............... | ,, | ,, | 0·1007 | 416 | 65·5 | 34·5 |

Leaving the product compositions and turning now to the rates themselves, we have to discuss the following fields of application of the theory of combined ionic-strength and mass-law effects in the unimolecular mechanism; *viz.*, (i) the effect of added " common-ion salts " on the initial rate of hydrolysis of those alkyl halides which exhibit a notable mass-law effect; and (ii) the whole kinetic course of the reactions of these alkyl halides in the presence of salts of all types : for we have seen that with " common-ion salts " both effects are present initially and throughout reaction, whilst with the " non-common-ion salts " the ionic-strength effect is present from the commencement and the mass-law effect is present at all times after the commencement of reaction. We may now consider these matters.

(d) *Initial reaction rates in the presence of " common-ion salts."* The formula, as given by our theory of the unimolecular mechanism, for the effect of added " common-ion salts " on the initial rate of hydrolysis of alkyl halides, follows by means of a simple modification of equation (14) :

$$k_1^{(c)}/k_1^{(0)} = \{\alpha^{(0)}c \text{ antilog}_{10}(- 1·815 \times 10^6 c^{\frac{1}{2}}/D^{3/2}T^{3/2}) + \text{antilog}_{10}(- 0·912 \times 10^{16}\sigma c/D^2 T^2)\}^{-1} \quad . \quad . \quad (19)$$

We already know the values of the ionic-strength constant $\sigma$ (Section 4), and we have made a previous approximate determination of the values of the mass-law constant $\alpha^{(0)}$ (Section 3). Therefore equation (19) enables us to calculate the ratios in which added " common-ion salts " should change the initial rates : we can compare the values so calculated with those observed.

This comparison is shown in Table VIII.* The agreement is not always very good, but is on the whole fair. In assessing it, one must remember that some of the $\alpha^{(0)}$ values

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* The best value of $\alpha^{(0)}$ for *tert.*-butyl bromide so far obtained being zero, we have used this value for the calculations of Table VIII, although it is practically certain that $\alpha^{(0)}$ has a small finite value, qualitatively corresponding to the finite degree of intervention by azide ions (this vol., p. 960).

3 x

have not yet been very accurately established, and that in some cases we are probably applying the theory outside the concentration range within which it may be expected to be valid. It will also be appreciated that, in all cases except that of *tert.*-butyl bromide, the mass-law effect is reducing the rate-ratios from much higher values, such as were listed in Table V (1·3—2·9) ; wherefore two figures like 0·93 and 1·08, although they are on opposite sides of unity, are not really in very serious disagreement.

TABLE VIII.

*Effect of " Common-ion Salts " on the Initial Rate of Hydrolysis of Alkyl Halides in Aqueous Acetone, and Comparison with Effect as calculated from the $\alpha^{(0)}$-Values of Section (3).*

| Alkyl halide. | Salt. | Conditions. | | | $10^5 k_1^{(c)}$. | $k_1^{(c)}/k_1^{(0)}$. | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | Solvent. | Temp. | $c$. | | Obs. | Calc. |
| Bu$^\gamma$Br .......................... | None | " 90% " | 50° | 0·0000 | 19·0 | — | — |
| ,, .......................... | LiBr | ,, | ,, | 0·1065 | 27·4 | 1·44 | 1·42 |
| Ph$_2$CHCl ...................... | None | " 80% " | 25 | 0·0000 | 7·45 | — | — |
| ,, ...................... | NaCl | ,, | ,, | 0·0190 | 7·23 | 0·97 | 0·97 |
| ,, ...................... | HCl | ,, | ,, | 0·0955 | 6·90 | 0·93 | 1·08 |
| Ph$_2$CHBr ...................... | None | " 90% " | 50 | 0·0000 | 201 | — | — |
| ,, ...................... | LiBr | ,, | ,, | · 0·1013 | 161 | 0·80 | 0·98 |
| Bu$^\gamma$·C$_6$H$_4$·CHPhCl ......... | None | " 80% " | 25 | 0·0000 | 76·0 | — | — |
| ,, ......... | NaCl | ,, | ,, | 0·1000 | 48·0 | 0·63 | 0·94 |
| Me·C$_6$H$_4$·CHPhCl ......... | None | ,, | ,, | 0·0000 | 160 | — | — |
| ,, ......... | NaCl | ,, | ,, | 0·0365 | 120 | 0·75 | 0·73 |
| ,, ......... | HCl | ,, | ,, | 0·0385 | 128 | 0·80 | 0·73 |
| ,, ......... | ,, | ,, | ,, | 0·0950 | 117 | 0·73 | 0·70 |
| (Me·C$_6$H$_4$)$_2$CHCl ............. | None | " 85% " | 0 | 0·0000 | 47·0 | — | — |
| ,, ............. | LiCl | ,, | ,, | 0·0555 | 23·0 | 0·49 | 0·58 |

(e) *The mass-law constant $\alpha^{(0)}$.* We may use the data of Table VIII for the purpose of computing additional values of the constant $\alpha^{(0)}$, in order to combine these values with those derived from the kinetic form of hydrolysis in the absence of salts in an endeavour to fix the constants more definitely. It does not seem possible to fix them very accurately, probably because we have in part worked with too large concentrations.* The available evidence is in Table IX.

The constant for benzhydryl bromide is evidently to be distinguished from the others, because it represents the competing efficacy of the bromide ion against water, whereas all the other constants represent the competing efficacy of chloride ions. Comparing the constants for benzhydryl chloride and bromide, we see that the bromide ion is about five times as active as the chloride ion in reaction with the benzhydryl cation. Comparing the chloride constants amongst themselves, we find an increase along the alkyl series given on p. 982; and this must correspond either to an increase of the average life of the alkyl cation, or to an increase in the vulnerability of its solvation shell. The second alternative seems very improbable, and, indeed, we would rather assume a decrease of vulnerability and an increase of average life large enough to constitute the preponderating influence.

(f) *Kinetic form of reactions in the presence of salts.* The theoretical kinetic form varies with the salt, the three chief cases being " common-ion salts," " non-common ion salts " whose intervention forms a product which is much more rapidly hydrolysed than the original alkyl halide, and " non-common ion salts " whose intervention forms a product that is not hydrolysed. In the first case we have ionic-strength and mass-law effects working

* It was realised only when we were part-way through the experimental programme that, although our theoretical formulæ hold for *tert.*-butyl bromide up to ionic strengths somewhat above 0·1, the limit of validity for benzhydryl and substituted benzhydryl halides is smaller, falling to about 0·04—0·05 in the case of dimethylbenzhydryl chloride. As the corrections which a second-approximation theory would introduce depend essentially on molecular size, we should have expected this greater restriction in the range of our formulæ, and reduced our concentrations accordingly as soon as we began to work with these larger molecules. However, although this adjustment was left rather late, we succeeded in carrying out a sufficiency of low-concentration experiments to illustrate all the principal applications of the formulæ before our stocks of alkylbenzhydryl halides became exhausted. For quantitative comparisons like those of sub-sections (5*b*) and (5*c*) it is obviously not important to maintain particularly low ionic strengths.

TABLE IX.

*Values of the Mass-law Constants $\alpha^{(0)}$.*

| Alkyl halide. | Method. | Salt. | Conditions. | | | $\alpha^{(0)}$. | Mean $\alpha^{(0)}$. |
| | | | Solvent. | Temp. | c (approx.). | | |
|---|---|---|---|---|---|---|---|
| Ph$_2$CHCl | 1 | — | "90%" | 50° | — | 10 | |
| | „ | — | "80%" | 25 | — | 10 | 11·5 |
| | 5 | NaCl | „ | „ | 0·02 | 10 | |
| | „ | HCl | „ | „ | 0·10 | 16 | |
| Ph$_2$CHBr | 1 | — | "90%" | 50 | — | 50 | 60 |
| | 5 | LiBr | „ | „ | 0·10 | 70 | |
| Bu$\gamma$·C$_6$H$_4$·CHPhCl | 1 | — | | „ | — | 20 | |
| | „ | — | "80%" | 25 | — | 20 | ~28 |
| | 5 | NaCl | „ | „ | 0·10 | 43 | |
| Me·C$_6$H$_4$·CHPhCl | 1 | — | „ | „ | — | 35 | |
| | 5 | NaCl | „ | „ | 0·04 | 33 | 32 |
| | „ | HCl | „ | „ | 0·04 | 28 | |
| | „ | HCl | | „ | 0·10 | 33 | |
| (Me·C$_6$H$_4$)$_2$CHCl | 1 | — | "90%" | 0 | — | 69 | |
| | „ | — | "85%" | „ | — | 69 | 74 |
| | „ | — | "80%" | „ | — | 69 | |
| | 5 | LiCl | "85%" | „ | 0·06 | 89 | |

together from the commencement of the reaction; in the last two we start with a pure ionic-strength effect and then observe a growing mass-law effect—of course modified by the ionic-strength effect, as well as superposed upon it, in accordance with the discussion of Section 3. Because of this modification, "non-common-ion salts" which yield a substitution product that immediately makes more ions by hydrolysis have to be distinguished from "non-common-ion salts" which yield a stable substitution product.

The formula for the rate of hydrolysis in the presence of "common-ion salts" is

$$\frac{dx}{dt} = \frac{k_1^{(0)}(a-x)}{\alpha^{(0)} . (c+x) \operatorname{antilog}_{10}\{-1\cdot815 \times 10^6(c+x)/DT^{3/2}\} + \operatorname{antilog}_{10}\{-0\cdot912 \times 10^{16}\sigma(c+x)/(DT)^2\}} \quad (20)$$

This involves only the mass-law and the ionic-strength constant, $\alpha^{(0)}$ and $\sigma$, appropriate to the alkyl halide itself. The equation for the rate of total reaction (measured as hydrolysis), of an alkyl halide RX, in the presence of a "non-common-ion salt" MY such that RY is hydrolysed much more rapidly than is RX, is

$$\frac{dx}{dt} = k_1^{(0)}(a-x) . \frac{1 + \alpha_Y^{(0)}c \operatorname{antilog}_{10}\{0\cdot912 \times 10^{16}\sigma_Y(c+x)/(DT)^2 - 1\cdot815 \times 10^6(c+x)^{\frac{1}{2}}/(DT)^{3/2}\}}{\alpha_X^{(0)}x + \alpha_Y^{(0)}c \operatorname{antilog}_{10}\{0\cdot912 \times 10^{16}(\sigma_Y - \sigma_X)(c+x)/(DT)^2 - 1\cdot815 \times 10^6(c \times x)^{\frac{1}{2}}/(DT)^{3/2}\} + \operatorname{antilog}_{10}\{-0\cdot912 \times 10^{16}\sigma_X(c+x)/(DT)^2\}} \quad (21)$$

This contains, not only the mass-law and the ionic-strength constant, $\alpha_X^{(0)}$ and $\sigma_X$, of the alkyl halide being hydrolysed, but also the corresponding constants, $\alpha_Y^{(0)}$ and $\sigma_Y$, of the compound RY; if RY is another of the investigated alkyl halides, we shall know all the constants necessary. The simultaneous equations for the rate, $dx/dt$, of the total reaction, and the rates of its constituents, viz., the rate of hydrolysis, $dx'/dt$, and the rate of anion attack, $dx''/dt$, for the case of an alkyl halide RX, reacting in the presence of a "non-common-ion salt" MZ such that RZ is not appreciably hydrolysed during the time of the experiment, are

$$\frac{dx}{dt} = k_1^{(0)}(a-x) . \frac{1 + \alpha_Z^{(0)}(c-x'') \operatorname{antilog}_{10}\{0\cdot912 \times 10^{16}\sigma_Z(c+x')/(DT)^2 - 1\cdot815 \times 10^6(c-x')^{\frac{1}{2}}/(DT)^{3/2}\}}{\alpha_X^{(0)}x + \alpha_Z^{(0)}(c-x'') \operatorname{antilog}_{10}\{0\cdot912 \times 10^{16}(\sigma_Z - \sigma_X)(c+x')/(DT)^2 - 1\cdot815 \times 10^6(c+x')^{\frac{1}{2}}/(DT)^{3/2}\} + \operatorname{antilog}_{10}\{-0\cdot912 \times 10^{16}\sigma_X(c+x')/(DT)^2\}}$$

$$\frac{dx'}{dt} = k_1^{(0)}(a-x) . \frac{1}{\text{Same denominator}}$$

$$\frac{dx''}{dt} = \frac{dx}{dt} - \frac{dx'}{dt}$$

$$\left.\begin{array}{c} \\ \\ \\ \\ \\ \end{array}\right\} \quad (22)$$

These equations also contain four constants, of which two, $\alpha_X^{(0)}$ and $\sigma_X$, can be considered known, whilst in principle we could use the fact that two of these equations are independent in order to determine the remaining constants, $\alpha_Z^{(0)}$ and $\sigma_Z$. The above equations can all directly be written down after a short inspection of equation (14). Like equation (14),

FIG. 8.

*Kinetics of Hydrolysis of* $0.0314$M-p-*Methylbenzhydryl Chloride in the Presence of* $0.0385$M-*Hydrogen Chloride in " 80% " Aqueous Acetone at 25°, and of* $0.0479$M-pp'-*Dimethylbenzhydryl Chloride in the Presence of* $0.0555$M-*Lithium Chloride in " 85% " Aqueous Acetone at 0°.*
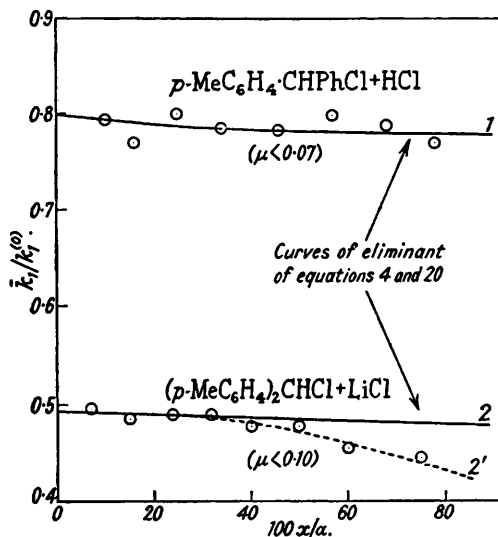


[*Curve* 1: ($\mu$, $0.0385 \rightarrow 0.0699$) $10^5\sigma = 2.22$, $a^{(0)} = 28$.  *Curve* 2: ($\mu$, $0.0555 \rightarrow 0.1034$) $10^5\sigma = 2.73$, $a^{(0)} = 89$.  In each case $a$, $c$, $D$ and $T$ for conditions stated.  *Curve* 2': experimental deviation from Curve 2.]

they should be applicable only to very dilute solution. In order to apply them to our results we have, as usual, to combine them with equation (4) after numerical integration.

FIG. 9.

*Kinetics of Hydrolysis of* $0.0979$M-*Benzhydryl Chloride in the Presence of* $0.0964$M-*Lithium Bromide in " 90% " Aqueous Acetone at 50°.*
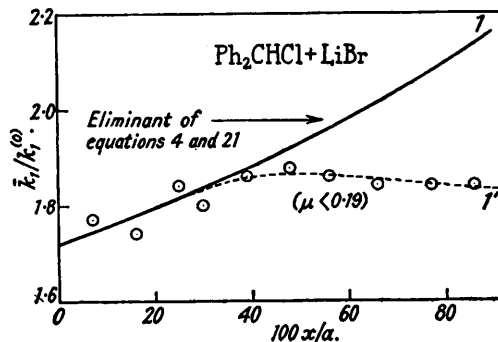


[*Curve* 1: ($\mu$, $0.0964 \rightarrow 0.1943$) $10^5\sigma_X = 1.38$, $10^5\sigma_Y = 1.74$, $\alpha_X^{(0)} = 11.5$, $\alpha_Y^{(0)} = 60$, $a$, $c$, $D$ and $T$ for conditions stated.  *Curve* 1': experimental deviation from Curve 1.]

Two examples of the application of the theory to our experiments on hydrolysis in the presence of a " common-ion salt " are represented in Fig. 8.  As usual, we plot against the

percentage progress of reaction, $100x/a$, the integrated first-order rate constants of the reaction in the presence of the salt, reckoned as a fraction of the initial specific rate of hydrolysis of the same alkyl halide in the absence of the salt, $\bar{k}_1/k_1{}^{(0)}$. The upper curve refers to an experiment with $p$-methylbenzhydryl chloride and hydrogen chloride, in which the ionic strength cannot rise above 0·07, and here we find the observed results to be consistent with the theoretical curve, the time-eliminant of equations (4) and (20). The lower curve relates to an experiment with $pp'$-dimethylbenzhydryl chloride and lithium chloride, in which the ionic strength can rise to 0·1 ; here we find consistency between the observations and the curve given by the same equations only during the first half of the reaction, and a growing inconsistency as the ionic strength approaches its maximum.

Fig. 9 illustrates the case of a " non-common-ion salt," the equations used being (4) and (21). The application is to an experiment with benzhydryl chloride and lithium bromide, in which the ionic strength can rise to 0·19. Corresponding to these relatively large ionic strengths, we find that the observations are consistent with the theoretical curve only in the initial stages of reaction, after which there is a strong deviation of just the type found in the simpler calculations, illustrated in Fig. 7, on *tert.*-butyl bromide with added salts at similar concentrations. It would appear that at these rather large ionic strengths our formulæ over-estimate the ionic-strength effect and require a negative correction, just as Debye's limiting theory of the activity coefficient of ions over-estimates their mutual influence at the larger ionic strengths and requires the reducing correction factor which the second approximation theory of Debye and Hückel supplies.

## (6—7) *Conclusions.*

(6) *Summary of New Evidence on the Unimolecular Mechanism of Nucleophilic Substitution.*—(a) *Solvolytic substitutions : kinetic form.* The experimental results analysed in the preceding sections relate mainly to solvolytic substitutions, *viz.*, the hydrolysis of certain alkyl halides in aqueous acetone. A study of the kinetic form of these reactions has provided an unambiguous demonstration of the existence and general nature of the unimolecular mechanism of such solvolytic substitutions. The proof depends on the circumstance that, because of the two-step character of the unimolecular mechanism, and particularly because of the reversibility of the first and rate-determining step, this mechanism requires a highly characteristic rate law : it reduces to a first-order rate law only as a limit, to which some examples may closely approximate, whilst others, differing from these according to rules that can be indicated, are expected to show considerable deviations of a distinctive and calculable form. Most of the reactions investigated showed considerable deviations from a first-order rate law; furthermore, these reactions exhibited just that particular form of kinetics which the unimolecular mechanism predicts. It is emphasised that the kinetic test is not one that will distinguish every unimolecular reaction, because a substitution may be entirely unimolecular and yet involve component processes whose relative rates are such as to preclude an observable departure, that would diagnose the mechanism, from first-order kinetics. But when such departures can be observed they are distinctive, and our applications of the test have indicated a sufficient number of unimolecular reactions to prove the importance of the mechanism in aliphatic substitution generally. It will be understood that the unimolecular mechanism, since it depends on ionisation, naturally presupposes an ionising solvent. Our present experiments have referred to acetone containing 10 or more vols. % of water ; but, as we have emphasised elsewhere, it is not at all impossible that the unimolecular mechanism may give place to the bimolecular mechanism near the limit of low water content. This, for example, *might* be the case in some of the moist acetone and moist dioxan solvents used by Taylor, even though, as we show in accompanying papers, his evidence that the bimolecular mechanism really does obtain under such conditions is quite valueless.*

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* (Added in proof.) Limiting forms of the mass-law effect introduce new connexions between reaction order and mechanism. For example, the just reported second-order kinetics of the reaction of $p$-methoxybenzhydryl chloride with low concentrations of methyl alcohol in nitrobenzene solutions, buffered to definite concentrations of chloride ions (Bartlett and Nebel, *J. Amer. Chem. Soc.*, 1940, **62,**

(b) *Solvolytic substitutions : salt effects on rate.* Further demonstrations arise from our study of the effect of added salts. In the first place, the unimolecular mechanism, on account of the rather simple character of its rate-determining step from a purely electrostatic point of view, requires that all added electrolytes will, by virtue of their contribution to the ionic strength of the solution, increase the reaction rate, and modify the kinetic form of substitution, to a characteristically large extent, and under quantitative laws, relating to the influence of concentration, solvent, and temperature, that can be calculated for dilute solution. These effects have been observed, and they are in quantitative accord with theory.

Secondly, on account of its two-step character and the reversibility of the first step, the unimolecular mechanism has the characteristic requirement that, in proportion as the reaction deviates from the first-order rate law in the absence of added salts, electrolytes whose anions are identical with that which the alkyl halide liberates on substitution will, in contradistinction to all other electrolytes, exert a superposed effect, which depresses the reaction rate and modifies the kinetic form of substitution under a further set of laws that can be calculated for dilute solutions. These effects have been observed. For dilute solutions they are in quantitative accord with theory, whilst for more concentrated solutions the deviations are in the predicted direction. Once again, this test is not bound to succeed with a unimolecular reaction. But when it does give positive results, these are diagnostic ; and positive results have been obtained in a sufficient number of examples to establish the general importance of the unimolecular mechanism.

(c) *Non-solvolytic substitutions : reaction rates.* The experiments already referred to automatically involved a study of the rates of reactions in which the halogen atom of the alkyl halide was replaced by the attack of the anions of the salts introduced into the aqueous medium : under these conditions such non-solvolytic substitutions accompanied the solvolytic reactions. The chief non-solvolytic substitutions studied involved the use of halide and azide ions as substituting agents. We have direct kinetic proof that those substitutions proceeded by the unimolecular mechanism, because the anionic substituting agents, apart from the effect of their contributions to the ionic strength, did not influence the rate of destruction of the alkyl halide, even when they were engaging in a large amount of substitution.

(d) *Solvolytic and non-solvolytic substitutions : product compositions.* Further confirmation of these conclusions, alike in relation to solvolytic and non-solvolytic substitutions, emerges from a study of the proportions in which the products are formed when the two kinds of substitution are in competition. One test is analogous to that which we have previously applied (J., 1938, 881) to competing solvolytic reactions in mixed solvents : it consists in finding whether the reaction rates and product compositions agree as they should if both are determined in the same (bimolecular) reaction stage. As with the former pairs of solvolytic reactions, so also with these competing solvolytic and non-solvolytic

1345), can be explained on any of the following mechanisms, of which the third involves a relationship between order and mechanism not elsewhere illustrated :

(1) Bimolecular nucleophilic substitution ($S_N2$), *i.e.*, attack by methyl alcohol at the saturated carbon atom with replacement in a single stage.

(2) Preliminary ionisation ($S_N1$), with no mass-law effect, but with a large solvent influence, initially proportional therefore to the (small) concentration of the active constituent, methyl alcohol (cf. this vol., p. 913) ; Bartlett and Nebel adopt a particularised form of this explanation when they suggest preliminary ionisation involving electrophilic catalysis by methyl alcohol (cf. this vol., p. 930), *i.e.*, a strongly selective attraction of this constituent for the halogen.

(3) Preliminary ionisation ($S_N1$), having no variable solvent influence, but a large mass-law effect :
for with [Cl⁻] constant, and [MeOH], as well as [RCl], small, the unimolecular system $RCl \underset{(2)}{\overset{(1)}{\rightleftharpoons}} R^+ +$ $Cl^- \xrightarrow[\text{MeOH}]{(3)}$ ROMe, etc., despite its slow ionisation, $v_1 \ll (v_2 + v_3)$, will require second-order kinetics if $v_2 \gg v_3$.

(4) Preliminary ionisation ($S_N1$), with solvent and mass-law effects of intermediate magnitude, aggregating to the effect of either alone in the limits (2) and (3).

We think that the reported retarding effect of a saline chloride indicates (3) or (4), but that a more detailed study is necessary to permit any positive statement concerning the mechanism of this substitution.
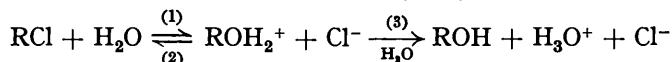
substitutions (hydrolysis and alkyl azide formation), we find that the reaction rates are controlled by a different reaction stage from that in which the products are formed.

The second test is analogous to that by which we have previously cross-checked independently reached conclusions that certain simultaneous substitutions and eliminations are each unimolecular ($S_N1$ and E1) in mechanism (J., 1937, 1277, 1280, 1283) : if the simultaneous processes have a common first step, in which the halogen atom removes itself before a competition determines the proportions of the products, then these proportions should remain unaltered when we change the halogen atom. Substantially, our previous experience was repeated, the proportions of the products of competing solvolytic and non-solvolytic substitutions (hydrolysis and alkyl azide formation) remaining unchanged when we changed the halogen of the alkyl halide. The implication is that the halogen removes itself before the substituting agents come upon the scene, as the unimolecular mechanism requires.

It is to be emphasised that these tests indicate the operation of the unimolecular mechanism *both* in hydrolysis and in substitution by reagent anions, since an incursion of the bimolecular mechanism into either substitution would have changed the experimental result.

(7) *Conclusions derived from New Evidence on the Unimolecular Mechanism.*—(a) *Existence and nature of the unimolecular mechanism.* The evidence summarised in the preceding section is of direct and largely quantitative character, leaving little scope for alternative explanations. Thus it is abundantly clear that the bimolecular mechanism, either of solvolytic or of non-solvolytic substitution, cannot accommodate any of the sets of observations which apply to these respective cases. However, it is interesting to consider what conclusions are necessary as a minimum, and what scope for variation still exists.

In the first place, the mass-law effect, even in its qualitative aspect, means that the mechanism of substitution involves more than one stage, that some earlier stage than the product-forming one is rate-determining, that some earlier stage than the product-forming one is reversible, and that one product of the reversible stage is the halide ion deriving from the alkyl halide. Most of the same conclusions are independently required to explain the results relating to product compositions. These conclusions already exclude any one-stage mechanism, but would allow us to increase the number of stages assumed in the unimolecular mechanism to more than two, and would allow us also to vary the hypothesis that the product complementary to the halide ion in the reversible stage is the (solvated) alkyl cation. However, this amount of liberty is greatly restricted in view of the quantitative success of the theory which assumes only a rate-determining, reversible ionisation, succeeded by a rapid formation of the substitution product : in these quantitative results there is nothing to indicate further complication, and much to exclude particular forms of complication. The only variation which seems worth a short consideration is that which allows covalency formation in the rate-determining stage :

$$\text{RCl} + \text{H}_2\text{O} \underset{(2)}{\overset{(1)}{\rightleftharpoons}} \text{ROH}_2^+ + \text{Cl}^- \xrightarrow[\text{H}_2\text{O}]{(3)} \text{ROH} + \text{H}_3\text{O}^+ + \text{Cl}^-$$

Apart from quantitative difficulties which need not be discussed, this scheme is rendered unacceptable by the circumstance that, since the alkyloxonium ion has to serve as intermediate both for solvolytic and for non-solvolytic substitution, of which process (2) is a prototype, the observable mass-law effect implies that a bimolecular substitution (*e.g.*, process 2) which involves the rupture of a C–O bond has to be credited with the same sort of instantaneity as a proton transfer (*e.g.*, process 3) from one oxygen atom to another. But we know the order of magnitude of the concentrations in which alkylhydroxonium ions are formed from alcohols under given conditions of acidity in aqueous solution, and this tells us that bimolecular nucleophilic substitutions of the type of process (2) are in fact measurably slow, as, indeed, process (2) itself would have to be (since the alkyloxonium ion can be generated from the alcohol) in order to permit the observation of an almost completely irreversible hydrolysis.*

* In this section we are taking account *only* of the evidence presented earlier in this paper. There is, however, much else that the scheme formulated would not explain, *e.g.*, why, if water is effective, hydroxide ions are ineffective; why partial or complete racemisation occurs; and why rates and product compositions in mixed solvents do not agree as they should on this theory in the example of the solvolysis of *tert.*-butyl chloride, in which the mass-law effect is small.

We confirm here that our investigation leads to identical conclusions for both solvolytic and non-solvolytic substitutions. This convenient if rather meaningless distinction has, in our opinion, been over-emphasised by some opponents of the idea of the unimolecular mechanism, who have limited their discussions to solvolytic substitutions, presumably because of the supposed immunity of these to kinetic diagnosis of the type by which, for certain non-solvolytic substitutions, the unimolecular mechanism has been established. We show here, however, that a refined kinetic analysis can deal with solvolytic substitutions also, and that it likewise establishes the unimolecular mechanism in certain cases. In the next two papers we supplement the kinetic evidence already existing in relation to non-solvolytic substitutions by the same more refined type of analysis; and we show that, once again, the ionic-strength and the mass-law effects, which in their qualitative and quantitative aspects distinguish the unimolecular mechanism, are prominent in selected cases. Thus for both types of substitution the evidence of mechanism is parallel, and equally significant.*

(b) *Detailed picture of the unimolecular mechanism : the ionisation* ("*Process* 1"). In the unimolecular mechanism the slow, and therefore rate-controlling, process is the ionisation of the alkyl halide. This is an activated process, involving passage of the system over a definite energy maximum at some critical separation of the dissociating particles. The maximum is caused by solvation, which also reduces its energy to thermally accessible values (Hughes and Ingold, J., 1935, 252), as has been illustrated very clearly in terms of crossing potential energy curves by Ogg and Polanyi (*Trans. Faraday Soc.*, 1935, **31**, 604).

The matter of solvation appears to have caused some difficulty. It has been pointed out by other authors that energies of ionisation must be of the order of 200 kg.-cals./g.-mol.—far higher, therefore, than any thermal activation energy accessible to a molecular system at the ordinary temperature : it has not always been made clear, however, that this statement refers only to *gaseous* ionisations (which explains why they never occur at the ordinary temperature). Possibly the difficulty has been to appreciate that solvation is not just a minor factor in the energy relationship, but is perfectly capable of supplying the whole of the necessary difference—itself amounting to something of the order of 200 kg.-cals./g.-mol. We can well understand this, because solvation can spontaneously break down the lattices of ionised crystals, whose lattice energies are of just this order (*e.g.*, 181 kg.-cals./g.-mol. for sodium chloride crystals). Nobody supposes that stable covalencies must necessarily be formed in order to supply this energy : almost the whole of it comes from the electrostatic and dispersive forces between the ions and the solvent. Similarly, it is not essential to assume that any stable covalencies are contemporaneously formed in order to explain where the energy comes from that enables the ionising bond of an alkyl halide to break. In bimolecular substitution the energy does come largely from a forming bond, but in unimolecular substitution the main source of the energy of ionisation is solvent affinity.†

Concerning the configuration of the system at the energy maximum, approximate calculations have shown that this involves the stretching of the original carbon-halogen bond by not much more than 0·5 A. For all separations beyond this relatively small

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* [Added 23.3.40.] Probably Balfe and Kenyon would accept this as a satisfactory reply to their suggestion (*J. Amer. Chem. Soc.*, 1940, **62**, 445) that, because Taylor and some others have drawn different conclusions from Bartlett, Hammett, Hückel, and ourselves with regard to solvolytic substitution, "the course of these reactions is not sufficiently simple to justify the application of the kinetic method."

† [Added 20.1.40.] One author (Ogg, *J. Amer. Chem. Soc.*, 1939, **61**, 1964) has raised the matter in a rather less crude form by claiming to have taken care of the solvation energy, and thus to have established by calculation that the activation energies demanded by the unimolecular mechanism would be at least 50 kg.-cals., and therefore still too great to admit of measurable rates at the ordinary temperature. But as Bartlett and Knox have pointed out (*ibid.*, p. 3184), Ogg's calculations apply primarily to the reactions of methyl halides in aqueous solutions, and for such substitutions no evidence that would indicate a unimolecular mechanism has yet been found; in any case, the calculations are too rough to signify, the uncertainties introduced being of the same order of magnitude as the quantities calculated.

amount, the molecule may, from an energetic, and therefore a kinetic, point of view, be considered ionised (Ingold, *Trans. Faraday Soc.*, 1938, **34**, 222). The point is of importance in relation to the evidence derived from studies on the stereochemical course of substitution (below).

Our picture of the transition state as involving an electrical transfer from one part of the dividing molecule to the other has been made the basis of a rate-law for ionisation, analogous to the Brönsted–Debye law for the rates of bimolecular interaction of ions. The activity correction in the rate-law for ionisation is an explicit function of experimental quantities, and of a molecular parameter, which for simple molecules can be roughly estimated from known molecular constants. This rate-law has been partly verified (cf. also the next paper but one). It may prove of service for the diagnosis of other rapidly succeeded ionisations, such as those postulated in the field of tautomerism and the correlated reversible additive reactions.

(c) *Detailed picture : ionic recombination* (" *Process 2* "). The present work provides the first definite evidence of the molecularity of this very rapid process : as might have been expected, it is bimolecular over-all, *i.e.*, unimolecular with respect to each of the participating ions.

We have also been able to prove (although the evidence is not presented here, as the point is being reserved for fuller treatment later) that the ionic recombination, in spite of its rapidity, is an activated process. This follows from observations on the temperature coefficient of the mass-law constant. Such observations determine $E_2 - E_3$, the difference in the activation energies of processes (2) and (3). This difference is finite and positive, wherefore, since no activation energy can be negative, the activation energy of process (2) must be finite and greater than a specificable minimum. The necessity for activation in both ionisation and ionic recombination is in agreement with the conception of an energy maximum for ionisations in solution.* Activation of the dissociating molecule is necessary, because it is only " beyond a certain degree of extension of the polarised link that the increasing solvation due to the separating electric charges contributes a fall of energy which is more rapid than the rise that would have occurred in the absence of solvation " (Hughes and Ingold, *loc. cit.*). Activation of the recombining ions is required for a corresponding reason, *viz.*, that their large solvation energy has to be partly compensated before the energy liberated in the forming bond is able to determine the completion of the bond-forming process.

(d) *Detailed picture : product formation in solvolytic substitution* (" *Process 3* "). The molecularity of this final, rapid stage of sovlolytic substitution has been determined in the case of hydrolysis : it is unimolecular with respect to the alkyl cation and multimolecular with respect to water. We should expect this : on account of the large energy requirements, many water molecules must contribute the solvation energy, and therefore many water molecules must be contained in the solvation shell of the alkyl cation ; and, given any necessary energy by thermal collision, this cation, plus its shell, contains all the elements of reactivity, and therefore need not depend for its destruction on being pierced by the attack of a single, energised water molecule.

We are trying to discover whether any thermal activation at all is needed, but as yet we only know that the activation energy of process 3 is in any event small. Thus a highly important determinant of the defect of the absolute rate below the collision frequency must be a very small phase factor, which in turn is to be attributed to the high molecularity.

The defect of the rate below the collision frequency, or, in other words, the time-lag between processes (1) and (3), is the most characteristic feature of the unimolecular mechanism : when this lag vanishes, then the unimolecular mechanism merges into the bimolecular mechanism. We have emphasised often before that the mechanisms do merge, *i.e.*, that there is no sharp dividing line between them. The absolute determination of the time-lag is still an unsolved problem, and at present we know only how to change it at will by means of structural alterations in the cation.

* This idea is implied in the theory of a common ion in tautomerism (Ingold, Shoppee, and Thorpe, J., 1927, 1481), since the known slowness of some ionic recombinations cannot then be attributed to a preliminary slow isomerisation of ions (cf. Ingold, *Trans. Faraday Soc.*, 1938, **34**, 226).

(e) *Detailed picture : product formation in non-solvolytic substitution (Process 2').* We have directly investigated the unimolecular replacement of the halogen atom of alkyl halides by an azide group, an azide ion being the substituting agent; and, more indirectly, the replacement of the halogen by another halogen atom, a halide ion being the substituting agent. The analogous rapid processes by which the final products are formed in these non-solvolytic substitutions have unit molecularity with respect to each of the participating ions. Furthermore, they are undoubtedly activated processes, as we have proved in the example of alkyl azide formation by a method analogous to that mentioned in section (c) above.

(f) *A note on nomenclature.* We think it desirable to refer to this subject because confusion could arise from the differing terminologies employed by different authors. Like ourselves, Farinacci and Hammett (*J. Amer. Chem. Soc.*, 1937, **59**, 2544) have previously emphasised the rôle of the solvent in effecting the ionisation of alkyl halides and the multiplicity of the necessary solvent molecules; and in order to signalise this aspect they have termed the ionisation, and therefore the whole solvolysis mechanism, "multi-molecular." On the other hand, we term the ionisation process, and hence the whole mechanism, "unimolecular," not because many molecules are not present in the transition state of the rate-determining process, but because only one molecule is necessarily under-going covalency change. Consistently we call the final process of cation hydroxylation "multimolecular" because of the kinetic evidence that, in the transition state of this process, many molecules are, not merely present, but necessarily undergoing covalency change. We prefer to define molecularity by the number of molecules necessarily involved in covalency change, since the alternative system, strictly applied, would make all reactions in solution multimolecular, the solvent being always present, in principle at least, in the transition states of reactions in solution. The result, however, is that Hammett and his collaborators and we are using the same word "multimolecular" for different things : this does not matter, provided the difference is understood.*

*Appendix (Added* 20/1/40) : *Present Position of the Earlier Evidence on the Unimolecular Mechanism.*

In the preceding discussion, mechanism of substitution is considered solely in the light of the evidence now presented for the first time. In order to give a more general picture we here review the earlier arguments in the light of these new facts and of contributions by other workers.

(a) *Dependence of Rate on the Constitution of the Alkyl Derivative (Method* 2).—There is little to add on this subject except that the new results confirm the old interpretation. First, we have general confirmation, inasmuch as the alkyl halides whose solvolysis the new results prove to have the unimolecular mechanism are compounds which belong on the right hand side of the rate minimum exhibited in a series arranged in order of increasing capacity for electron release by the alkyl groups. Secondly, we find detailed confirmation, in that the order found amongst alkyl groups for the mass-law constant, $\alpha$, which measures the stability of the alkyl cation in the environment associated with solvolysis, agrees in detail with the order of electron release by the alkyl groups investigated.

(b) *Dependence of Rate on the Constitution of the Substituting Agent (Method* 3).—This was the basis of the second of Hughes, Ingold, and Patel's two original arguments (J., 1933, 526), the point chiefly stressed being the dependence of rate on the basicity of the substi-tuting agent in the bimolecular mechanism, and its independence of basicity in the uni-molecular process. The value of this simple criterion is emphasised in the present work, as it will be still further when we publish our control research on kinetic and salt effects in the bimolecular mechanism.

(c) *Solvent Effects on Rates and Product Compositions (Method* 4).—Fuller explanation is necessary in relation to solvent effects, inasmuch as conflicting views have recently arisen. The first contribution was made by Olson and Halford (*J. Amer. Chem. Soc.*, 1937,

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* Hückel, whose views (*Annalen*, 1939, **540**, 278) agree with ours in most essentials, does not, how-ever, stress the multiplicity of solvent molecules needed for ionisation.

**59**, 2644), who took the point of view that all solvolyses of alkyl halides were bimolecular. Having replaced the concentration rate-equation for a bimolecular reaction by a vapour pressure rate-equation, they suggested that the relationship

$$\text{Rate} = (k_a p_a + k_w p_w) p_{RX}$$

should express the total rate of solvolysis of an alkyl halide, such as *tert.*-butyl chloride (RX), in a mixture of solvents, such as methyl alcohol (*a*) and water (*w*), the partial rates of formation of the separate products, ROMe and ROH, being $k_a p_a p_{RX}$ and $k_w p_w p_{RX}$ respectively (the $p$'s are vapour pressures). After having determined the disposable constants, $k_a$ and $k_w$, from measured total rates at two extremes of solvent composition, the authors showed that their formula satisfactorily represented the total rates at intermediate solvent compositions. From this they concluded that the mechanism was bimolecular. Then we pointed out (Bateman, Hughes, and Ingold, J., 1938, 881) that the success of their formula for rate interpolation owes nothing to the assumed mechanism : what its success does depend on has since been discussed by Bartlett (*J. Amer. Chem. Soc.*, 1939, **61**, 1630). We further showed that the correct way of using the formula for the purpose of deriving conclusions relative to mechanism was to determine whether the proportions in which ROMe and ROH were formed could be calculated by means of the same pair of constants, $k_a$ and $k_w$, whose values had been fixed by means of rate determinations : if rates and products were determined in the same reaction stage, whose mechanism was supposed known, this should be possible, but not, of course, if rates and products were determined in different reaction stages. In the case considered there were large discrepancies, and similar discrepancies had already appeared in the work of Farinacci and Hammett in the analogous example of benzhydryl chloride (*ibid.*, 1937, **59**, 2544; cf. Bateman, Hughes, and Ingold, *ibid.*, 1938, **60**, 3080). It followed that the solvolysis was not the one-stage, bimolecular replacement process which Olson and Halford had imagined. The results were, however, consistent with the two-stage unimolecular mechanism, which requires no direct connexion between reaction rates and product compositions, since these are determined in different reaction stages.

Winstein has recently suggested (*ibid.*, 1939, **61**, 1635) that Olson and Halford's rate formula should be applied on the basis of an assumed one-stage, termolecular or quadrimolecular replacement process, the reaction complex involving two or three hydroxylic molecules. He claimed that this treatment brings rates and product composition into harmony. However, the approximate agreement obtained is unimpressive for the following reason. The Olson–Halford formulæ for ter- and quadri-molecular replacement reactions may be written

$$\text{Rate} = (k_{aa} p_a^2 + k_{aw} p_a p_w + k_{ww} p_w^2) p_{RX}$$
$$\text{Rate} = (k_{aaa} p_a^3 + k_{aaw} p_a^2 p_w + k_{aww} p_a p_w^2 + k_{www} p_w^3) p_{RX}$$

in which the various constants, $k_{aa}$, etc., can in principle be determined by measuring the total rate at a sufficient number of different solvent compositions. It is, however, a difficulty with all formulæ of this kind that product compositions cannot be calculated on the basis of these constants only : for, corresponding to each interior (mixed-subscript) term of either polynominal, it is necessary for the calculation of product compositions to adopt a value for yet another, unknown constant, *viz.*, the partition ratio which governs the break-down of a reaction complex of type RX + $H_2O$ + MeOH, RX + $2H_2O$ + MeOH, RX + $H_2O$ + 2MeOH, to form the products ROH and ROMe. These extra constants can only be adjusted by reference to the product-compositions themselves; and, since for each particular set of substances (RX, *a* and *w*) our experimental data provided no more than three product-compositions to be fitted, each requiring a toleration of some units % on account of experimental error, the fitting process is, with this large power of adjustment, neither difficult nor significant. Notwithstanding the latitude indicated, and the further assistance obtained from an unacceptable treatment of our experimental results,* the
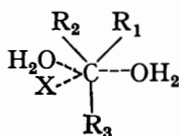
* The olefinic reaction product was reckoned as equivalent to ether, instead of as alkyl halide diverted from substitution processes.

agreement produced by the formula for a termolecular reaction was not always within the observational error in the determination of product compositions.

These arguments have been made dependent on Olson and Halford's rate equation partly because, although we remarked on the difficulty of its inconsistency with the transition state theory, we were unwilling to shift the basis of discussion from that adopted by Olson and Halford whilst reversing these authors' conclusions. However, as Professor Hammett has urged in correspondence with us, an improved treatment founded on the rate equation of Brönsted, Polanyi, and Eyring is very desirable. Recently such a treatment has been carried through by Bartlett (*loc. cit.*). He came to the conclusion, as Hammett and we did, that the bimolecular mechanism is definitely inadmissible; and he went further than we did in showing that the variation of product composition with solvent composition is consistent with the requirements of the unimolecular mechanism. The new treatment does not go further than the old in excluding Winstein's idea of a one-stage, ter- or quadri-molecular replacement process; but then it would not be unfair to ask the author of this view to base on it as coherent a picture of the other groups of facts* as has been based on our idea of replacement in the second stage of the unimolecular mechanism.

(d) *Stereochemical Course of Substitution (Method 6).*—In this matter also divergent views have arisen. We made the distinction that, whilst nucleophilic bimolecular substitution always leads to a complete inversion of configuration, unimolecular substitution leads either to racemisation, possibly with some inversion, or, in the presence of a group which suitably binds the cationic centre, to retention of configuration, possibly with some racemisation (Cowdrey, Hughes, Ignold, Masterman, and Scott, J., 1937, 1252).

In the former case, the partial inversion was interpreted as an effect of the partial shielding of the cation by the receding anion, which, for the less stable cations, may not be many molecular diameters away when the attack of the solvent takes place; and what we know of the effect of structure on the degree of completeness of racemisation in substitutions of this kind is entirely consistent with the idea that the effect is one on the stability of the cation : the more stable the latter, the more complete the racemisation. Winstein has objected to this explanation (*loc. cit.*). He says : " If ionisation were complete enough to permit the reaction to be called unimolecular, then the ion $R^+$ would be free enough from shielding effects so that a completely racemic product would result." However, our answer to this had already been given (Ingold, *Trans. Faraday Soc.*, 1938, **34**, 222) : ionisation is " complete enough to permit the reaction to be called unimolecular " so soon as the system of separating charges has passed over its energy barrier (cf. p. 1006), and this, as we have seen, may occur at separations which exceed the normal covalency length by not much more than 0·5 A. (cf. p. 985).† Winstein's idea is to construct transition states, as illustrated in the inset, for ter- or quadri-molecular replacement in one stage, and by means of these to accommodate either retention of configuration, or inversion, or racemisation by ejecting appropriate particles. However, as we have already pointed out in a slightly different connexion (Cowdrey, *et al.*, *loc. cit.*), such transition states will be much less stable than the "linear" states characteristic of bimolecular substitution, because of the large positive exchange integrals between the electrons of the non-linearly split bond and those of the full bonds.

Concerning the stereochemical outcome of substitution in the presence of a group, such as an $\alpha$-carboxylate ion group, which can bind a cationic centre, our view was that the solvent rather than the group causes the formation of the centre ($S_N1$), but that the group then holds it with a bond of mainly electrostatic character pending solvent attack. This is in contrast to the effect of $\beta$- and $\gamma$-carboxylate ion groups, where in the simplest cases

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* Notably the mass-law (" common-ion ") effect, which, though only now described in detail, was announced in 1938 (Bateman, Hughes, and Ingold, *J. Amer. Chem. Soc.*, 1938, **60**, 3080).

† The conception of shielding is not inconsistent with the conclusion that a free carbonium is flat. Bartlett and Knox (*loc. cit.*) regard flattening as necessary for the existence of an alkyl cation, having shown that neither the bimolecular nor the unimolecular mechanism of substitution is available to a molecule for which neither inversion nor the flattening of the ion can occur.

no cationic centre is formed,* since the group becomes the substituting agent ($S_N2$) and directly establishes a bond of mainly covalent character (*i.e.*, forms a lactone) (*idem, ibid.*). The older view, which neglected duplexity of mechanism in substitution generally, extended the $S_N2$-type of explanation to the case of the α-group (cf., *e.g.*, Bancroft and Davies, *J. Chem. Phys.*, 1931, **35**, 1253; Young and Olson, *J. Amer. Chem. Soc.*, 1936, **58**, 1157), and this idea has been revived by Winstein and Lucas (*ibid.*, 1939, **61**, 1567; cf. Winstein, *loc. cit.*). However, it seems to us to involve a definite loss of consistency, for reasons which appear more cogent than those we originally advanced, when we bring the strong electron repulsion of the α-carboxylate ion group, and the relatively small activity of halides containing this group towards powerful bases, into the related body of considerations, the general validity of which our new work confirms. It should be emphasised that the real point is, not at what stage in the range of constitutions possible for a bond of mixed covalent-ionic character the ring which it completes should be called a " lactone," but whether the completion of the ring is a one-stage process ($S_N2$) or a two-stage process involving the preliminary ionisation of the halogen ($S_N1$). As we originally stated, even the bond formed by the α-carboxylate ion group, which completes the ring that we termed a " betaine," has some covalent character; and, correspondingly, our views accommodate the interpretation given by Winstein and Lucas (*ibid.*, pp. 1576, 1581, and 2845) to the case they have discovered of a substitution involving an intermediate cation preserved as to configuration by an α-bromine atom : here the symmetry of the systems converts, through resonance, what would have been a dipole with one covalent and one electrostatic bond into a ring with two equivalent bonds which are partly covalent and partly electrostatic. We have amplified our previously expressed views on this question, because it is less academic than in 1937, our new work on the distinction between the $S_N1$ and $S_N2$ mechanisms in intermolecular substitution having opened up new and definite criteria for the operation of the same two mechanisms in the slightly more difficult field of internal substitution. Indeed, significant kinetic differences between the cases of α- and more remote carboxylate-ion groups have already been established. Winstein and Lucas used no such sharp criteria, which alone could have justified conclusions contrary to the trend of the circumstantial evidence.

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