190. *Mechanism of Substitution at a Saturated Carbon Atom. Part XXV. Unimolecular Halogen Exchange between an Alkyl Halide and Halide Ions in Sulphur Dioxide Solution; and a Concluding Note.*

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The reactions of fluoride and iodide ions with *m*-chlorobenzhydryl chloride in sulphur dioxide have been further investigated (cf. p. 1011), and the former substitution has been subjected to detailed study. This reaction follows neither a first- nor a second-order law, but, on the other hand, exhibits the peculiar kinetics of the unimolecular mechanism (cf. p. 979). The agreement with theory is quantitative.

The kinetics of the unimolecular mechanism embody two features, *viz.*, an ionic-strength effect which is characteristically large, and a mass-law effect which is entirely characteristic. The reaction now studied has the special interest that these effects can be very easily separated and each studied without interference from the other.

The ionic strength is unusually large, partly because the reaction is unimolecular and partly because the dielectric constant of sulphur dioxide is rather small. It is observed, without interference from the mass-law effect, by studying the variation of initial rate with fluoride-ion concentration. An ionic strength of 0·05 trebles the rate. The effect is of the calculated magnitude, and its dependence on concentration in dilute solution accurately obeys the e^{μ}-law deduced for an ionisation (cf. this vol., p. 979).

The mass-law effect, in which chloride ions, by reversing the ionisation of the alkyl halide, retard substitution independently of any reversal of the substitution process, is very large indeed. It entirely controls the kinetic form of substitution, since the ionic strength does not change in the course of the reaction. Owing to the decelerating influence of the developing chloride ions, a reaction which starts quickly ends relatively slowly. The same effect, superposed on, but completely dominating, the ionic-

strength effect is observed in the influence of initially added chloride ions on the initial reaction rate. Concentrations of added chloride no larger than 0·04M have produced mass-law effects depressing the rate by factors down to 1/150. All these effects show that chloride ions attack the alkyl cation 20 times faster than fluoride ions.

THE survey described in the preceding paper yielded a qualitative indication that the nucleophilic substitutions of benzhydryl halides in sulphur dioxide proceed by the unimolecular mechanism. It also suggested the halogen exchanges and Menschutkin reactions of *m*-chlorobenzhydryl chloride as suitable subjects for quantitative kinetic investigation. In this paper we record such an investigation for halogen exchange: our quantitative work on the Menschutkin reaction has been delayed, and will be reported later.

(1) *Kinetics of the Reaction between* m-*Chlorobenzhydryl Chloride and Fluoride Ions.*

The most convenient halogen exchange for quantitative study was found to be the reaction of *m*-chlorobenzhydryl chloride with fluoride ions supplied in the form of tetramethylammonium fluoride. Tetramethylammonium chloride, which is produced in the reaction, is soluble in the solvent, and hence the solution remains homogeneous. Furthermore, under these conditions the exchange

$$RCl + F^- \underset{(b)}{\overset{(a)}{\rightleftharpoons}} RF + Cl^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (I)$$

proceeds to an equilibrium which is well over on the right—sufficiently far, at least, to enable a considerable proportion of the reaction to be followed without appreciable disturbance from the retrograde process. If substitution occurs by the unimolecular mechanism, we can understand an equilibrium situated as described, since the more facile ionisation of RCl than of RF will favour reaction (I*a*).

(a) *Qualitative Explanation of the Kinetics.*—The reaction was followed by means of measurements of electrical conductivity, controlled by chemical analysis.

The reaction–time curves indicated a complicated form of kinetics, not expressed by any classical reaction order. If the mechanism of substitution were unimolecular, we should expect this; for, as explained in a preceding group of papers (this vol., pp. 960, 966, 971, 974, 979), the first-order rate law is a limiting law for unimolecular substitution, and is, in general, more or less markedly disobeyed on account of two effects, *viz.*, a mass-law effect which is entirely characteristic of the unimolecular mechanism, and an ionic-strength effect, which, although not qualitatively characteristic, is especially large in the unimolecular mechanism.

Setting out the forward component (*a*) of reaction (I) in accordance with the unimolecular mechanism,

$$RCl \underset{(2)}{\overset{(1)}{\rightleftharpoons}} R^+ + Cl^- \xrightarrow[F^-]{(3)} RF + Cl^- \quad . \; . \; . \; . \; . \; . \quad (Ia)$$

we see that a mass-law effect will arise provided that the rate of reaction (2) is not negligibly small in comparison with that of reaction (3). As, actually, the rate constant of reaction (2) is considerably greater than that of reaction (3), the mass-law effect becomes very large. The result of it may be described as follows. The cation, R^+, is formed from RCl according to a first-order rate law. Assuming that the only solutes initially present are the reagents RCl and F^-, of reaction (Ia), it can be asserted that, initially, the whole of the R^+ formed will be converted into RF. But at all times after the commencement of reaction the formed R^+ will become partitioned, a part yielding RF and the remainder being reconverted into RCl; and the fraction of the R^+ formed that passes into RF will fall progressively as an increasing concentration of chloride ions is built up. Thus the observed rate of formation of RF will fall in a progressively increasing degree below the rate at which R^+ is being formed, *i.e.*, below the rate of a first-order reaction.

The ionic-strength effect consists, strictly, in a modification of the rates of all of the component reactions, (1), (2), and (3), on account of the ionic environment. We can show, however, that, owing to the similar nature of reactions (2) and (3), the effect of the ionic atmosphere on their rates will be nearly equivalent, so that it is a justifiable approximation to treat the ratio in which R^+ is partitioned between reactions (2) and (3) as independent of the ionic strength. In this approximation, therefore, the discussion of the ionic-strength effect on the whole substitution process (Ia) reduces to a consideration of the effect of ionic strength on the rate-controlling ionisation (1). The rate of any ionisation of a neutral molecule must increase with the ionic strength, because an ion atmosphere reduces the energy of the transition state of ionisation, which is a strong electric dipole. For dilute solutions the law of the increase is known, and even the value of the single molecular parameter which it contains is approximately known.

Concerning the separation of the two effects, we have already observed that, if the only solutes present initially are the reagents of process (Ia), the mass-law effect does not disturb the initial rate. Therefore, by the study of initial rates with different concentrations of the tetramethylammonium fluoride, we can isolate the ionic-strength effect. We now note also that in any one substitution experiment the ionic strength will be independent of the time (because substitution merely replaces one halide ion by another). It follows that the ionic-strength effect will not disturb the *form* of the reaction–time curve, a study of which will isolate the mass-law effect. Of course, the ionic strength will modify absolute rate throughout reaction, but only by a constant factor; so that, if we deduce from the whole reaction–time curve the rate-constant for the rate-governing reaction (1), we shall obtain the same dependence on ionic strength as if we had evaluated the constant directly from the initial rate of substitution.

There is another way to isolate the mass-law effect, *viz.*, by the measurement of initial rates in the presence of initially added tetramethylammonium chloride. If, for reference, we make an initial rate measurement in which the only initial solutes are *m*-chlorobenzhydryl chloride and tetramethylammonium fluoride, and then repeat it with the initial addition of tetramethylammonium chloride, the mass-law effect due to the added chloride ions should decrease the rate, certainly below the enhanced value appropriate to the increased ionic strength, and possibly below the original value. Because the mass-law effect is large, we actually observe rates depressed to far below the original value. The depressions, as reckoned from the enhanced rates corresponding to the ionic strengths, directly measure the mass-law effect.

Naturally the mass-law effect will control the general form of the reaction–time curve in these experiments with initially added tetramethylammonium chloride, just as in experiments without an initial addition of this salt; and in both cases the mass-law effect will be the sole determinant of kinetic form, provided the reaction does not go so far towards equilibrium that we can no longer neglect the retrograde substitution process (I*b*).

The mass-law effects are definite proof of the unimolecular mechanism of substitution. The agreement of the ionic-strength effect with calculation is corroborative evidence; as is also the rough identity of the rates of substitution with different substituting agents, as established in our preliminary, semi-quantitative survey (preceding paper).

(b) *Ionic-strength Effect.*—The stabilisation by means of an ionic atmosphere of the transition state may be expressed also as a diminution in its fugacity or activity, and measured by the defect of a corresponding activity coefficient below unity; and the relationship with activation energy is such that, on the transition state theory of reaction rate, the ionisation should be accelerated by a factor which is simply the reciprocal of this activity coefficient. The activity coefficient, f_T, has to be derived from a consideration of an electrical interaction limited by thermal motion: it depends on the ionising molecule only through an electrical parameter, σ, of the transition state, on the ionic environment only through the ionic strength, μ, on the solvent only through its dielectric constant, D, and otherwise only on the absolute temperature T (*loc. cit.*):

$$(1/f_T) = \text{antilog}_{10}(0{\cdot}912 \times 10^{16}\sigma\mu/D^2T^2) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It follows that, for our solvent and temperature ($D = 16{\cdot}4$ and $T = 262°$), the rate constant, $k_1^{(\mu)}$, of ionisation, in a solution in which the ionic strength is μ, is related to the limiting value, $k_1^{(0)}$, to which this constant tends as the ionic strength approaches zero, in the manner represented by the equation

$$k_1^{(\mu)} = k_1^{(0)}\,\text{antilog}_{10}(4{\cdot}94 \times 10^8\sigma\mu) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This is a limiting law for dilute solutions. We expect it to hold up to ionic strengths of about 0·04—0·05 (*loc. cit.*), after which deviations should arise which should cause the observed values of $k_1^{(\mu)}$ to fall below those calculated from this equation.

(c) *Ionic-strength Effect and Initial Rates.*—We have seen that by measuring initial, specific rates of substitution, $k_{t=0}^{(c)} = \{-(\text{d[RCl]}/\text{d}t)/[\text{RCl}]\}_{t=0}$, with different initial concentrations, c, of tetramethylammonium fluoride, we measure, directly and without disturbance, the ionisation rate constants, $k_1^{(\mu)}$, appropriate to the ionic strength, $\mu = c$, due to the tetramethylammonium fluoride. A number of measurements of the initial specific rates are assembled in Table I. The meaning of the fourth and fifth columns will be made clear in the experimental section: they have to do with the conversion of electrical conductivities into concentrations; the headings of the remaining columns are self-explanatory. We note that the salt effect on rate is enormous—far larger than for any known reaction in water; thus a salinity of only N/20 more than trebles the rate. This was expected: it arises in part from the unimolecular nature of the reaction, and in part from the relatively small dielectric constant of sulphur dioxide, and the inverse-quadratic effect of this represented in equation (1). On the other hand, there is no possibility of confusing the rate increase with the effect of a predominantly bimolecular reaction, since the factor by which the concentration of tetramethylammonium fluoride is changed over the range of experiments recorded is as high as 18.

TABLE I.

Initial Specific Rates ($k_{t=0}^{(c)}$ *in sec.*$^{-1}$) *of Substitution of* m-*Chlorobenzhydryl Chloride* (RCl) *by means of Tetramethylammonium Fluoride in Sulphur Dioxide at* — 10·75°.

Expt. No.	$a =$ $[\text{RCl}]_{t=0}$.	$c =$ $[\text{NMe}_4\text{F}]_{t=0}$.	$10^8\left(\frac{d\kappa}{dt}\right)_{t=0}$.	$\left(\frac{dx}{d\kappa}\right)_c$.	$10^6\left(\frac{dx}{dt}\right)_{t=0}$.	$10^5k_{t=0}^{(c)}$.
1	0·0670	0·0028	3·31	48·3	1·60	2·38
2	0·0683	0·0087	3·97	48·4	1·92	2·82
3	0·0692	0·0190	5·70	48·6	2·77	4·00
4	0·0651	0·0253	6·58	49·0	3·12	4·80
5	0·0683	0·0502	10·35	50·8	5·26	7·70

It follows from equation (2) that if we plot log $k_{t=0}^{(c)}$ (= log $k_1^{(\mu)}$) against c (= μ), we should get a straight line. Its intercept on the axis of ordinates should give the initial specific rate of substitution, that is, the rate constant of ionisation, corrected to indefinitely small ionic strengths. Its slope, $4{\cdot}94 \times 10^8\sigma$, should give the parameter σ.

The plot is shown in Fig. 1. Evidently the dependence of the initial rate of substitution on the concentration of the saline reagent is following a law of the form required by our interpretation of the effect as a neutral salt influence on an ionisation process. It is even satisfactory that the linear law is beginning to fail, as it should (and in the manner in which it should), at the largest ionic strength investigated.

The intercept of the straight line on the axis of ordinates gives $k_{t=0}^{(0)} = 2{\cdot}19 \times 10^{-5}$sec.$^{-1}$. This is interpreted as the rate constant, $k_1^{(0)}$, of ionisation in solutions of vanishingly small ionic strength. The slope of the straight line, which measures the intensity of the whole effect, gives for the parameter, σ, the value $2{\cdot}72 \times 10^{-8}$ cm. = 2·72 A.; and we have to consider whether this is a reasonable value. It will be recalled (*loc. cit.*) that if, when calculating f_T, we treat the transition state as a pair of point charges, $\pm ze$, separated by a distance, d, then σ is simply z^2d; although for any actual transition state, we have to absorb into σ a numerical factor, of the order of unity, to take account of the shape of the system. An order-of-magnitude calculation has been made (*loc. cit.*), which shows that, for any benzhydryl halide, σ should be of the order of 2 A.; and previous experience (*loc. cit.*) in connexion with the solvolytic reactions of various simple and substituted benzhydryl halides in aqueous acetone has given experimental values of σ, which vary from one halide to another but lie within the range 1·61 A. to 2·73 A. Thus the value which we here deduce from the non-solvolytic substitution of *m*-chlorobenzhydryl chloride in sulphur dioxide seems reasonable in the light of both theory and experience.

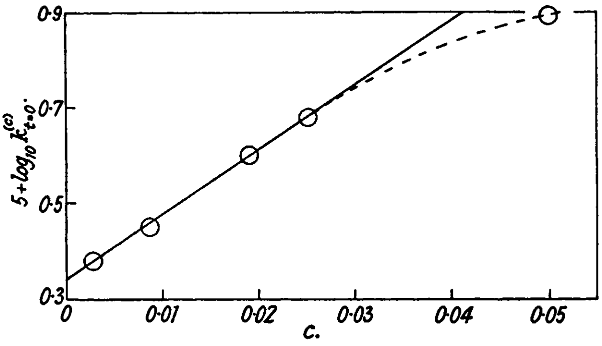
(d) *Mass-law Effect.*—In order to obtain a complete expression for the mass-law effect, we refer back to equation (Ia), and note that the measured rate of substitution is given by

$$dx/dt = v = v_1 v_3/(v_2 + v_3) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where v_1, v_2, and v_3 are the instantaneous rates of the component reactions (1), (2), and (3) respectively. For generality, let the initial concentrations of *m*-chlorobenzhydryl chloride, tetramethylammonium chloride and tetramethylammonium fluoride be *a*, *b*, and *c* respectively; the case in which no tetramethylammonium chloride is added initially can then easily be treated by setting *b* equal to zero. Referring to equation (1) above, and to equations (6) and (8) of our previous paper (this vol., p. 988), we find

FIG. 1.

Ionic-strength Effect on Initial Reaction Rate.



[The points show the observed dependence of the initial specific rate of substitution, $k_{t=0}^{(c)}$, of *m*-chlorobenzhydryl chloride by means of tetramethylammonium fluoride on the concentration, *c*, of the latter. The straight line shows the theoretical limiting form of the dependence for low salt concentrations, according to the interpretation that the rate variations represent an ionic-strength effect in unimolecular substitution.]

$$v_1 = k_1^{(0)}(a - x)\ \text{antilog}_{10}\{0{\cdot}912 \times 10^{16}\sigma(b + c)/D^2T^2\} \quad . \quad . \quad . \quad . \quad (4)$$

$$v_2 = k_2^{(0)}[\mathrm{R}^+](b + x)\ .\ \frac{\text{antilog}_{10}\{0{\cdot}912 \times 10^{16}\sigma(b + c)/D^2T^2\}}{\text{antilog}_{10}\{3{\cdot}63 \times 10^6(b + c)^{\frac{1}{2}}/D^{3/2}T^{3/2}\}} \quad . \quad . \quad . \quad (5)$$

$$v_3 = k_3^{(0)}[\mathrm{R}^+](c - x)\ .\ \frac{\text{antilog}_{10}\{0{\cdot}912 \times 10^{16}\sigma'(b + c)/D^2T^2\}}{\text{antilog}_{10}\{3{\cdot}63 \times 10^6(b + c)^{\frac{1}{2}}/D^{3/2}T^{3/2}\}} \quad . \quad . \quad (6)$$

Equation (6) contains the parameter, σ', for the transition state of ionisation of *m*-chlorobenzhydryl fluoride. We have not yet been able to determine this constant, but it cannot be very different from the constant, σ, relating to benzhydryl chloride. In our previous work we found that the values of σ for benzhydryl chloride and benzhydryl bromide differed by only 8%, and a model calculation showed that a difference of this order of magnitude should have been expected (*loc. cit.*). Analogous considerations suggest a similarly small difference between the constants for *m*-chlorobenzhydryl fluoride and chloride; and, because the rates are not very sensitive to the exact values of the constants,*

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* This is primarily because an antilogarithmic factor is equivalent to an exponential: if x is small, e^x may be approximated as $1 + x$, which suffers a proportionally smaller change than x, when x is varied. The application to equations (4—6) will be obvious.

we shall introduce no serious error by setting σ' equal to σ. Substituting equations (4), (5), and (6) in equation (3), and making this approximation, we find

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1^{(0)}\,\text{antilog}_{10}\{0{\cdot}912 \times 10^{16}\sigma(b + c)/D^2T^2\}\,.\,\frac{(a - x)(c - x)}{\alpha(b + x) + (c - x)} \quad . \quad (7)$$

where the " mass-law constant,"

$$\alpha = k_2^{(0)}/k_3^{(0)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

represents the ratio, at vanishingly small ionic strengths, of the speeds of attack by chloride and fluoride ions on the alkyl cation, R$^+$. Recalling equations (1) and (2), equation (7) may be rewritten

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1^{(\mu)}\,.\,\frac{(a - x)(c - x)}{\alpha(b + x) + (c - x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $k_1^{(\mu)}$ is given by equation (2), with $\mu = b + c$, $k_1^{(0)} = 2{\cdot}19 \times 10^{-5}$ sec.$^{-1}$, and $\sigma = 2{\cdot}72 \times 10^{-8}$. On integrating equation (9) we obtain

$$k_1^{(\mu)} = \frac{1}{t(a - c)}\left[\alpha(b + c)\log_e\frac{c}{c - x} + \{(a - c) - \alpha(a + b)\}\log_e\frac{a}{a - x}\right] \quad (10)$$

These equations illustrate a number of qualitative remarks made earlier. Thus equation (9) shows that the rate, $\mathrm{d}x/\mathrm{d}t$, is changed by the ionic strength only through the factor $k_1^{(\mu)}/k_1^{(0)}$, which is independent of x, and therefore remains constant throughout any one experiment. Equation (10) shows that the functional connexion between x and t, and, in particular, its deviation from the limiting first-order function,* depends only on the mass-law effect, *i.e.*, on α; although the value of the deducible constant, $k_1^{(\mu)}$, will depend on the ionic-strength effect, *i.e.*, on σ. Again, if we take the limiting form of equation (9) when t tends to zero, we obtain

$$\left\{\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_{t=0}\Big/a\right\}^{(\mu)} = k_1^{(\mu)}\,.\,\frac{c}{\alpha b + c}$$

or, in case $b = 0$,

$$\left\{\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_{t=0}\Big/a\right\}^{(\mu)}_{b=0} = k_1^{(\mu)}$$

This means that, if two measurements of the initial specific rate of substitution are carried out at the same ionic strength μ, in one only of which tetramethylammonium chloride is present, in concentration b, then this rate will be depressed below the other by the factor $c/(\alpha b + c)$. Measurement of this " rate-depression factor " (" RDF "), defined by

$$(\text{RDF}) = \left\{\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_{t=0}\Big/a\right\}^{(\mu)}\Big/k_1^{(\mu)} = \frac{c}{\alpha b + c} \quad . \quad . \quad . \quad . \quad (11)$$

thus gives an easy means of determining α.

(e) *Mass-law Effect and Initial Rates in the Presence of a Common Ion.*—Some determinations by this method of the mass-law constant, α, are recorded in Table II. Columns 2—5 give the initial concentrations and ionic strengths. The next two columns, which can be understood with the aid of experimental particulars given later, concern the translation of electrical conductivities into concentrations. The eighth column records the derived initial specific rates. The ninth gives the rates with which these have to be compared, *viz.*, rates for the same ionic strength but in the absence of tetramethylammonium chloride, as obtained by interpolation from the date of Table I. The factors by which the added tetramethylammonium chloride has depressed the rate are in the penultimate column, whilst the last column gives the values of α, which are derived from these factors by means of equation (11).

* $k_1^{(\mu)} = (1/t)\log_e\{a/(a - x)\}$. Naturally, this results from (10) when α is set equal to zero.

TABLE II.

Initial Specific Rates [$(\mathrm{d}x/\mathrm{d}t)_{t=0}/a$ *in sec.*$^{-1}$] *of Substitution of* m-*Chlorobenzhydryl Chloride* (RCl) *by Means of Tetramethylammonium Fluoride in the Presence of Tetramethylammonium Chloride in Sulphur Dioxide at* — 10·75°.

Expt. No.	$a =$ $[\mathrm{RCl}]_{t=0}$.	$b =$ $[\mathrm{NMe_4Cl}]_{t=0}$.	$c =$ $[\mathrm{NMe_4Cl}]_{t=0}$.	$\mu =$ $b + c$.	$10^8\left(\frac{\mathrm{d}\kappa}{\mathrm{d}t}\right)_{t=0}$.	$\left(\frac{\mathrm{d}x}{\mathrm{d}\kappa}\right)_{\mu}$.	$10^5\left\{\frac{\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_{t=0}^{(\mu)}}{a}\right\}$.	$10^5 k_1^{(\mu)}$.	"RDF."	α.
6	0·0671	0·0079	0·0032	0·0111	0·0811	48·4	0·0585	3·08	0·0190	20·9
7	0·0662	0·0065	0·0051	0·0116	0·186	48·4	0·136	3·12	0·0437	17·2
8	0·0650	0·0399	0·0057	0·0456	0·0607	50·4	0·050	7·50	0·00667	21·3
									Mean	19·8

The α-values are only approximately consistent, but the degree of agreement seems reasonable when it is reflected that they are obtained from rates depressed by factors ranging from 1/23 to 1/150, and that the kinetics are not highly sensitive to the precise value of α.

We may compare these effects of a salt having an anion in common with that produced from the benzhydryl halide with those which were observed in the solvolysis of such halides in aqueous acetone (*loc. cit.*). The largest rate depression found in solvolysis was in the case of *pp'*-dimethylbenzhydryl chloride, for which the addition of 0·05N-chloride ion reduced the substitution rate below that appropriate to the ionic strength in the absence of an added common ion, by the factor 1/3. In the present study of non-solvolytic substitution of *m*-chlorobenzhydryl chloride, the addition of 0·04N-chloride ions reduced the rate by the factor 1/150. The evident explanation of the difference is that chloride ions find less difficulty in competing for the alkyl cation with a substituting agent, such as fluoride ion, which is present as a solute in low concentration, than with a substituting agent, such as water, which forms an important constituent of the solvent.

(f) *Mass-law Effect and Kinetic Form of Substitution.*—The large influence of the mass-law effect is immediately apparent on inspection of the reaction–time curves. A part of one of these curves is exhibited in Fig. 2; it represents the first 20% of reaction, and experience has shown that, although the reversibility of the stoicheiometric substitution is not negligible over the whole of the observable reaction, its influence can be safely neglected over ranges of the order of that mentioned.* The common characteristic of all these curves is the contrast between their strong initial curvature and their slight subsequent curvature. No ordinary kinetic equation can be made to fit such curves; for example, if first- or second-order equations are fitted to the initial portion of the curve drawn in Fig. 2, these equations will not then fit the remainder of the curve; this is illustrated in the Fig. On the other hand, having determined the mass-law constant, α, from the effect of added chloride ions on the initial rate of substitution, we can proceed to show that equation (10), which expresses the special kinetic form required by the unimolecular mechanism, represents the kinetic form satisfactorily. The full-line curve of Fig. 2 is, indeed, the curve of equation (10), and it is practically identical with the best curve that can be drawn through the experimental points. It is to be noted that no use has been made of the kinetic form of substitution in deriving the constants, α and $k_1^{(\mu)}$, of equation (10)—these constants having been obtained entirely from observations of initial rates.

An alternative method of representation corresponds to that which we adopted in connexion with the solvolytic experiment (*loc. cit.*). First, from the readings obtained in an experiment, we calculate formally, either integrated first-order "constants," $\bar{k}_1$, or integrated second-order "constants," $\bar{k}_2$: these are, of course, not constant, but fall

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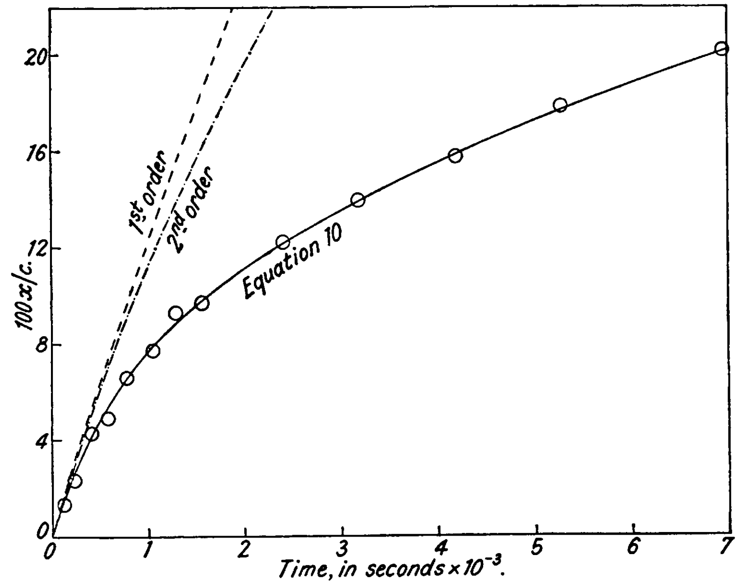
* These substitutions are considerably more reversible than the solvolytic substitutions in aqueous acetone (*loc. cit.*). Under the conditions of most of our experiments in sulphur dioxide, several units % at least of *m*-chlorobenzhydryl chloride and fluoride ions remained in pseudo-equilibrium with their reaction products; but it was found impossible to determine equilibrium compositions accurately, because the long experiments in which it was attempted to approach closely to equilibrium were subject to some slowly developing disturbance, which may have been a decomposition of benzhydryl fluoride analogous to the known decomposition of benzyl fluoride (Ingold and Ingold, J., 1928, 2249).

FIG. 2.

Kinetic Form of Substitution : Part of Reaction–Time Curve.



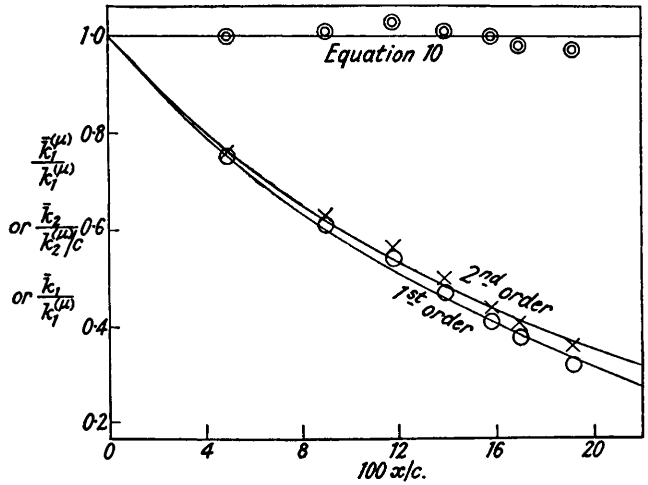
[The circles represent the observations of Expt. 4. The full-line curve is the graph of equation (10), with a, b, and c corresponding to concentrations used in Expt. 4, and k_1 and α taken from Tables I and II, respectively. The other curves represent the first- and second-order equations,

$$k_1t = 2{\cdot}303 \log\{a/(a - x)\} \text{ and } k_2t = 2{\cdot}303 \log\{c(a - x)/a(c - x)\}/(a - c),$$

fitted to the first part of the experimental reaction–time curve.]

FIG. 3.

Kinetic Form of Substitution : Integrated Rate Constants.



[○ Integrated first-order rate constants, k_1, from Expt. 1, with $k_1^{(\mu)} = 2{\cdot}38 \times 10^{-5}$ sec.$^{-1}$ as unity (Table I). Associated graph shows calculated dependence of these constants on reaction progress (equation 10).

× Integrated second-order rate constants, $\bar{k}_2$, from Expt. 1, with $k_1^{(\mu)}/c = 8{\cdot}50 \times 10^{-3}$ sec.$^{-1}$ g.-mol.$^{-1}$ l. as unity. Associated graph shows calculated dependence of these constants on reaction progress (equation 10).

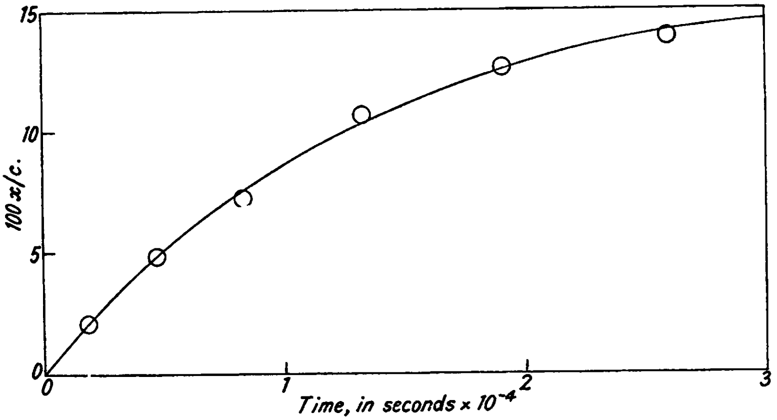
◎ Integrated "unimolecular" constants, $\bar{k}_1^{(\mu)}$, from Expt. 1, with $k_1^{(\mu)} = 2{\cdot}38 \times 10^{-5}$ sec.$^{-1}$ as unity. Equation 10 requires that these values should be constant and equal to unity.]

with the progress of the reaction. Then, by eliminating the time between equation (10) and the integrated rate equation for a first- or a second-order reaction, we can calculate the laws according to which these constants should fall if the kinetics were governed by equation (10). This is illustrated in Fig. 3, in which the curves associated with the points for the integrated first- and second-order rate constants, as calculated from the observations, are the theoretical curves obtained by the use of equation (10). On the other hand, if we calculate the integrate values, $\bar{k}_1^{(\mu)}$, of $k_1^{(\mu)}$, the rate constant of ionisation, directly from the observations by means of equation (10), we obtain the comparatively steady series of points shown at the top of the diagram.

It is obvious from either of these diagrams that substitution does not proceed by the bimolecular mechanism (S_N2), which would require a close approximation to second-order kinetics.* On the other hand, the observed kinetic form of substitution reveals all the quantitative features that particularly distinguish the unimolecular mechanism (S_N1).

FIG. 4.

Kinetic Form in Presence of Chloride : Part of Reaction–Time Curve.



[The circles represent the observations of Expt. 6. The curve is the graph of equation (10), with *a*, *b*, and *c* corresponding to the concentrations used in Expt. 6, and k_1 and α taken from Tables I and II respectively.]

(g) *Mass-law Effect and Kinetic Form in the Presence of Added Chloride.*—The primary influence of an initial addition of chloride ions is to depress the whole reaction rate strongly, owing to the mass-law effect of chloride ions which is characteristic of the unimolecular mechanism. But because the initial addition partly buffers the chloride-ion concentration, we expect the further depression of specific rate during the progress of reaction to be less marked than when no chloride is added initially. This means that there should be not nearly so much contrast between the initial and the later curvature of the reaction–time curve. This is illustrated in Fig. 4, which shows such a curve over a range within which it is safe to neglect the effect of the stoicheiometric reversibility of substitution. Actually the curve drawn is a graph of equation (10), which is hardly distinguishable from the best curve through the experimental points. It is thus clear that the equation of the unimolecular mechanism accounts quantitatively for the change of kinetic form described.

In spite of the more normal appearance of the reaction–time curves obtained in the presence of added chloride they are far from representing a reaction of any simple order. This is shown in Fig. 5, from which it is seen that integrated first- and second-order rate constants fall to about half their initial value after only 15% of the stoicheiometrically

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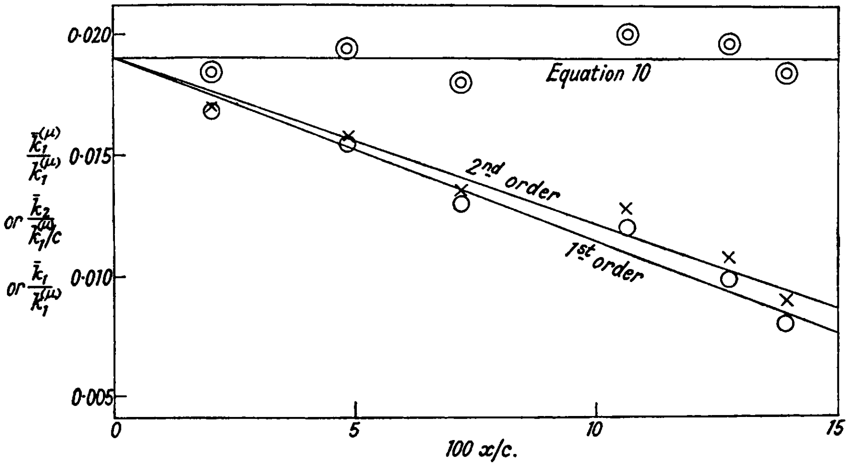
* The only cause for deviation would be an ionic-strength effect, which in the Brönsted–Debye approximation, would be zero, and which in any case should be small. (The Brönsted–Debye approximation in the kinetics of bimolecular reactions of ions corresponds to the approximation in which we treat unimolecular ionisation; *loc. cit.*)

possible reaction. Once again this can be quantitatively interpreted by means of equation (10) : it is simply the mass-law effect of the unimolecular mechanism (S_N1).

FIG. 5.

Kinetic Form in Presence of Chloride : Integrated Rate Constants.



[○ Integrated first-order rate constants, $\bar{k}_1$, from Expt. 6, with $k_1^{(\mu)} = 3{\cdot}08 \times 10^{-5}$ sec.$^{-1}$ as unity.
× Integrated second-order rate constants, $\bar{k}_2$, from Expt. 6, with $k_1^{(\mu)}/c = 9{\cdot}63 \times 10^{-3}$ sec.$^{-1}$ g.-mol.$^{-1}$ l. as unity.
◎ Integrated unimolecular rate constants, $\bar{k}_1^{(\mu)}$, from Expt. 6, with $k_1^{(\mu)} = 3{\cdot}08 \times 10^{-5}$ sec.$^{-1}$ as unity.
The curves are derived from equation (10) as previously illustrated.]

(2) *Reaction of* m-*Chlorobenzhydryl Chloride with Iodide Ions.*

We were unable to study this reaction in a quantitative manner because chloride and iodide ions made too nearly similar contributions to the conductivity. It was, furthermore, suspected that in homogeneous solution the equilibrium

$$\mathrm{RCl} + \mathrm{I}^- \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \mathrm{RI} + \mathrm{Cl}^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (\mathrm{II})$$

would be unfavourable to the study of the forward reaction (II*a*), because the more facile ionisation of RI than of RCl would favour reaction (II*b*). We tried overcoming these difficulties by supplying, as a source of iodide ions, a salt such that the corresponding chloride is very sparingly soluble, and is therefore precipitated with the result that reaction (II*b*) is inhibited and reaction (II*a*) allowed to proceed. Ammonium iodide fulfilled these conditions, but it proved unsatisfactory to have solid matter forming in the path of the current during measurements of electrical conductivity, and we therefore do not record our determined rate constants, since they cannot have more than a semiquantitative significance. For what it is worth, the figure found for the specific rate of substitution at $-10{\cdot}75°$ in the region of zero ionic strength was $k_1^{(0)} = 3{\cdot}3 \times 10^{-5}$ sec.$^{-1}$, but this is subject to considerable uncertainty.

(3) *Concluding Note.*

The group of consecutive papers of which this is the last have been presented together because they seem to us together to constitute a definite stage in our investigations of aliphatic substitution. We may here explain in what respect we suppose the general position to have been advanced.

First, in the course of the work now described, we considered it necessary to digress from the normal line of development in order to dispose of an obviously ill-founded, but nevertheless persistent, series of criticisms by Taylor, which at an earlier stage we had hoped to ignore, since they were largely self-inculpatory. The conclusions were easily demonstrated to be false. Moreover, in so far as we repeated the experimental work, we found nearly all of it to be incorrect; and the interal evidence of the part of the record that still remains unchecked shows that it is unlikely to come through a detailed re-examination more creditably.

Secondly, having thus " cleaned the slate "—for no unanswered criticisms of our conclusions now remain *—we felt free to continue the main investigation, the next stage of which was to develop for selected cases a somewhat careful proof of the ionisation mechanism. We deemed this necessary, not because we found the previous, less direct evidence unconvincing, but because of our belief that advance over the broad field of organic reactions would be greatly assisted by a more wide-spread recognition of the importance of ionisation as a mechanism of change, even in cases in which the equilibrium proportion of ions is immeasurably small or inaccessible to measurement. (We may here report that benzhydryl, *m*-chlorobenzhydryl and even *pp'*-dimethylbenzhydryl chlorides exhibit in sulphur dioxide no conductivity which was measurable in our apparatus.) We look upon Hughes and Ingold's work (since 1933) on aliphatic substitution, and their attempt (1937) to show that the facts of the Walden inversion required duplexity of mechanism involving such ionisation, as isolated instances only of the wide potential applicability of the ionisation theory. Our new proof was developed first for solvolytic substitutions, because this has been the chosen theatre of opposition to the theory; but we then showed that the same method of proof could also be applied, with identical results, to non-solvolytic substitutions—and thus to substitutions generally. This is where the matter now stands, but it is a legitimate hope that essentially the same methods will lead to equally clear-cut demonstrations in a number of fields—additions, eliminations, and isomeric changes—wherein the evidence of ionisation as a mechanism is still largely circumstantial.

EXPERIMENTAL.

Materials.—The preparative work is described in the preceding paper.

Apparatus.—This was the same as that described in the preceding paper, except that a different cell was used. The cell constant was determined by comparison with a standard cell at 25°, the same 0·01N-potassium chloride solution being used. The constant was originally 0·555 cm.$^{-1}$, but, after a minor accident and its repair, became changed to 0·570 cm.$^{-1}$. The conductivities recorded below (ohm^{-1} cm.$^{-1}$) are the measured reciprocal resistances, multiplied by the appropriate cell constant (distinction from the record in the preceding paper). The thermostat was set to $-10{\cdot}75°$.

Conversion of Conductivities to Concentrations.—For the experiments with tetramethylammonium fluoride as substituting agent it was necessary to know the conductivity change associated with the replacement of this salt by tetramethylammonium chloride at any constant total-salt concentration within the experimental range. The first step was to prepare conductivity–concentration curves for the two salts. For this purpose a portion of the dried salt was emptied quickly (without weighing) into the cell, and the sulphur dioxide was distilled on to it at $-$ 80°. When the cell had warmed to the thermostat temperature, the resistance was read and the volume of the solution noted. The sulphur dioxide was then evaporated, the salt dissolved in water, and the halide ion estimated. Fluoride ion was estimated by precipitation of lead fluoride chloride, which was collected, redissolved and estimated as chloride by Volhard's method (Mitchell and Ward, " Modern Methods in Quantitative Analysis," 1932, p. 77). The chloride ion was estimated by Volhard's method. These analyses, combined with the volume measurements, gave the concentrations corresponding to the observed conductivities.

The results, which are in Table III, when plotted yield two lines of different slope, passing through the origin, and having slight and similar curvatures towards the concentration axis

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* Except one by Roberts and Urey (*J. Amer. Chem. Soc.*, 1939, **61**, 2584) on the subject of esterification, which, being rather aside from the main theme, will be considered later. [Added 22/6/40.] Exception must also be made of a further paper by Taylor which has just appeared (this vol., p. 679). In it he claims to have realised hydrolysis of α-phenylethyl chloride with predominating retention of configuration, but the experimental evidence is unsatisfactory, and the conclusion anomalous.

(axis by abscissæ). By plotting the vertical separation of these curves against the abscissæ, we can obtain a curve for the conductivity difference between the salts at various concentrations. This curve is a straight line passing through the origin for concentrations up to 0·02, after which the line bends a little in the direction of the concentration axis. Taking now the ratios of the abscissæ to the ordinates of points along this curve, and plotting them against the abscissæ, we obtain a curve which gives, for each total-salt concentration, the factors by which conductivity changes are to be multiplied in order to give the concentrations of tetramethylammonium fluoride which have become replaced by tetramethylammonium chloride. The factors are substantially independent of the salt concentration up to 0·02, and then rise slightly; they are given in Table IV.

For the experiments with ammonium iodide as substituting agent it was necessary to have only the connexion between the conductivity of this salt and its concentration, since the formed ammonium chloride is precipitated. Ammonium iodide is not particularly hygroscopic and therefore could conveniently be weighed into the cell. In two cases, however, the concentrations derived by weighing the salt were checked by analysis, by methods similar to those of the calibration experiments with the tetramethylammonium salts. The results are in Table III. When plotted, they yield a line which passes through the origin and has a distinct curvature towards the concentration axis.

TABLE III.

Conductivity (κ *in* ohm^{-1} $cm.^{-1}$) *of Salts in Sulphur Dioxide at* — 10·75°.

NMe_4F.		NMe_4Cl.		NH_4I.	
$10^3\kappa$.	Concn.	$10^3\kappa$.	Concn.	$10^3\kappa$.	Concn.
0·289	0·0046	0·712	0·0079	0·203	0·0025 *
0·324	0·0053	0·940	0·0109	0·325	0·00485 * 0·00477 †
1·10	0·0163	2·16	0·0250	0·429	0·0074 *
1·30	0·0215	2·65	0·0328	0·587	0·0107 * 0·0106 †
2·92	0·0516	2·69	0·0341		
3·26	0·0601	3·03	0·0389		
3·88	0·0734	5·14	0·0719		
4·14	0·0794				

* By weighing. † By analysis.

TABLE IV.

Factors (dx/dκ) *for the Conversion of Conductivity Differences into Concentration of Reacted Tetramethylammonium Fluoride at Different Total-salt Concentrations* (μ).

μ	0·00	0·01	0·02	0·03	0·04	0·05	0·06	0·07
$dx/d\kappa$	48·3	48·4	48·7	49·2	49·9	50·8	51·8	53·0

Kinetic Measurements.—The salt was first introduced into the cell, and the sulphur dioxide was distilled on to it. When the solution had taken the temperature of the thermostat, — 10·75°, the volume and conductivity were noted. The *m*-chlorobenzhydryl chloride was added from a small graduated pipette. The immediate effect of this was to produce a fall of conductivity, owing presumably to the slight alteration in the properties of the ionising solvent. Thereafter the conductivity changed steadily, and readings were taken at suitable intervals. The results are in Table V.

TABLE V.

Changes of Conductivity (κ *in* ohm^{-1} $cm.^{-1}$) *during Reaction of* m-*Chlorobenzhydryl Chloride* (RCl) *with Fluoride Ions in Sulphur Dioxide at* — 10·75°.*

Expt. 1. Initially, [RCl] = 0·0670M, [NMe_4F] = 0·0028M.

t (mins.).	$10^4\kappa$.	t (mins.).	$10^4\kappa$.	t (mins.).	$10^4\kappa$.	t (mins.).	$10^4\kappa$.
0·0	2·017	11·3	2·037	27·5	2·081	69·0	2·136
1·9	1·974	13·2	2·044	33·0	2·091	81·0	2·146
4·4	1·998	17·6	2·057	44·8	2·109	127·0	2·172
6·3	2·013	20·4	2·065	51·0	2·118	180·0	2·181
8·6	2·026	23·8	2·072	60·5	2·128	258·0	2·190

TABLE V (*continued*).

Expt. 2. Initially, [RCl] = 0·0683M, [NMe$_4$F] = 0·0087M.

t (mins.).	$10^3\kappa$.	t (mins.).	$10^3\kappa$.	t (mins.).	$10^3\kappa$.	t (mins.).	$10^3\kappa$.
0·0	0·577	10·7	0·569	33·7	0·584	107·0	0·603
2·1	0·558	13·9	0·572	38·0	0·586	131·0	0·606
3·6	0·560	17·1	0·574	43·5	0·587	185·0	0·612
4·9	0·562	20·8	0·576	52·5	0·591	254·0	0·617
6·4	0·564	24·9	0·579	64·5	0·594	312·0	0·620
8·6	0·566	28·5	0·581	74·0	0·596	362·0	0·622

Expt. 3. Initially, [RCl] = 0·0692M, [NMe$_4$F] = 0·0190M.

t (mins.).	$10^3\kappa$.	t (mins.).	$10^3\kappa$.	t (mins.).	$10^3\kappa$.	t (mins.).	$10^3\kappa$.
0·0	1·225	10·2	1·193	48·1	1·233	228·0	1·290
1·6	1·176	15·6	1·201	73·5	1·248	285·0	1·297
3·7	1·186	22·7	1·212	103·5	1·260	363·0	1·309
7·1	1·189	33·5	1·223	159·0	1·276	443·0	1·315

Expt. 4. Initially, [RCl] = 0·0651M, [NMe$_4$F] = 0·0253M.

t (mins.).	$10^3\kappa$.	t (mins.).	$10^3\kappa$.	t (mins.).	$10^3\kappa$.	t (mins.).	$10^3\kappa$.
0·0	1·586	13·1	1·548	40·0	1·577	116·0	1·618
2·0	1·521	17·5	1·554	53·0	1·586	152·0	1·628
4·0	1·525	21·5	1·562	70·0	1·597	194·0	1·637
6·8	1·536	26·0	1·564	88·0	1·606	250·0	1·650
9·7	1·539	—	—	—	—	336·0	1·664

Expt. 5. Initially, [RCl] = 0·0683M, [NMe$_4$F] = 0·0502M.

t (mins.).	$10^3\kappa$.	t (mins.).	$10^3\kappa$.	t (mins.).	$10^3\kappa$.	t (mins.).	$10^3\kappa$.
0·0	2·861	10·8	2·775	45·0	2·839	124·0	2·898
1·6	2·741	16·1	2·789	57·0	2·854	193·0	2·932
3·4	2·749	23·0	2·803	73·0	2·868	260·0	2·965
6·5	2·762	32·0	2·817	95·0	2·883	363·0	2·985

Expt. 6. Initially, [RCl] = 0·0671M, [NMe$_4$F] = 0·0032M, [NMe$_4$Cl] = 0·0079M.

t (hrs.).	$10^4\kappa$.	t (hrs.).	$10^4\kappa$.	t (hrs.).	$10^4\kappa$.	t (hrs.).	$10^4\kappa$.
0·00	9·328	2·33	8·923	5·30	8·958	8·90	8·980
0·50	8·890	3·70	8·945	7·20	8·966	22·5	8·995
1·31	8·908	—	—	—	—	31·0	9·010

Expt. 7. Initially, [RCl] = 0·0662M, [NMe$_4$F] = 0·0051M, [NMe$_4$Cl] = 0·0065M.

t (hrs.).	$10^4\kappa$.	t (hrs.).	$10^4\kappa$.	t (hrs.).	$10^4\kappa$.	t (hrs.).	$10^4\kappa$.
0·00	9·208	0·58	8·856	3·50	8·962	7·8	9·028
0·06	8·824	1·58	8·806	4·50	8·982	23·0	9·069
0·25	8·836	2·59	8·935	5·50	8·997	31·0	9·076

Expt. 8. Initially, [RCl] = 0·0650M, [NMe$_4$F] = 0·0057M, [NMe$_4$Cl] = 0·0399M.

t (hrs.).	$10^4\kappa$.	t (hrs.).	$10^4\kappa$.	t (hrs.).	$10^4\kappa$.	t (hrs.).	$10^4\kappa$.
0·00	33·550	3·1	33·159	7·1	33·216	9·1	33·236
0·18	33·101	5·6	33·187	8·1	33·226	9·6	33·238
2·50	33·140	—	—	—	—	48·0	33·384

* In this Table the conductivities at zero time are those measured *before* the introduction of the alkyl chloride.

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