240. *Mechanism of Substitution at a Saturated Carbon Atom. Part LVIII.* Mechanism of S_N1 Substitutions in a Solvent of Low Solvating Power. A Comparative Discussion.*

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Whilst the results and internal conclusions of the preceding four papers agree in indicating that in each a substitution of S_N1 type is under survey, a comparison of all the results and conclusions reveals a total kinetic pattern sufficiently unprecedented to show that the details of the S_N1 mechanism become significantly modified in solvent benzene.

We have rates of substitution of a common substrate which do not depend on the concentration of the reagent, but do depend on its nature. In concurrent substitutions, we find evidence of competition for a slowly produced intermediate by the reagents, but with competing efficiencies which do not follow the rates of their independent substitutions. We have catalysis of inconstant kinetic order by many polar molecules, including molecular reagents, of all the substitutions, whether by anionic or molecular reagents, and the anionic substitutions are catalysed the more strongly; so that, when an anionic and a molecular substitution are run concurrently, an increase in the concentration of the molecular reagent diverts the primary reaction away from substitution by that reagent. We have strong catalysis by non-reacting salts, particularly perchlorate, of the molecular substitutions; and this catalysis is subject to competitive effects, which show that the active catalyst, kinetically indicated to be the simple perchlorate ion, is attacking a slowly formed intermediate; that is, it is intervening after a slow step, and yet it is providing a by-pass to a rate-controlling step. Finally, such catalysis does not apply at all to the anionic substitutions, which, if affected, are anticatalysed by perchlorate.

This group of results, from any conventional viewpoint largely a collection of paradoxes, is discussed theoretically. It is pointed out that the customary mechanistic deductions from the kinetic form, including mass-law retardation, of S_N1 substitutions is illogically specialised, and that the logically justified, and more general, deductions would include mechanistic modifications capable of accommodating the relations described. These relations are rationalised on the particular basis that S_N1 substitutions in benzene involve two slow, jointly rate-controlling steps, with an intervening fast, product-controlling step. More precisely, a slow ionisation, not entailing dissociation, is succeeded by a fast dipole association, and thereafter by a slow quadrupole rearrangement. The first two steps correspond to the two steps of that more familiar type of S_N1 substitution which prevails in highly solvating solvents; but these steps become modified by the low solvating power of solvent benzene. The modifications render the third step necessary, which therefore owes its existence, and its kinetic significance, to the low solvating power of the solvent. The energetics of the various steps are discussed, and it is shown that the expected energies are physically reasonable, and consistent with experiment.

THE immediately preceding four papers, which deal severally with the nucleophilic substitution of triphenylmethyl chloride by chloride ion, azide ion, methyl alcohol, and benzyl alcohol, in solvent benzene, each presents a kinetic picture pointing to an S_N1-type mechanism. Yet, when we compare results among the different papers, we discover kinetic features, which are not encountered in those S_N1 substitutions with which we

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* Part LVII, preceding paper.

are most familiar, and which are, indeed, not easy to understand on the basis of the simple formulation usually given to the S_N1 mechanism. We cannot therefore be content just to label our reactions S_N1, and leave the matter there. Some important difference to the detail of this mechanism must have been made when we transferred the reactions to be studied from hydroxylic solvents to solvent benzene. In this paper we try to deduce the nature of the difference. The first step is to get the observations into a single perspective.

(1) *Review of the Observations.*—In this section we shall set down in summary, not all the observations, but all that are relevant to the ensuing argument. The first group relates primarily to the reaction of ***chloride exchange***, the substituting agent being tetra-*n*-butylammonium radiochloride (Part LIV).

(C 1) The exchange is of first order in triphenylmethyl chloride, and of zeroth order in the salt. No evidence could be found for a concurrent bimolecular exchange. A bimolecular exchange with the ion-pair as reagent would have produced a kinetic order of unity in salt, and one with the free chloride ion as reagent, an order of one-half in salt; but the order was accurately zero.

(C 2) The specific rates of chloride exchange at 25°, 30°, and 44·6° respectively are 0·320, 0·503, and $1·68 \times 10^{-5}$ sec.$^{-1}$. The Arrhenius activation energy is 16·0 kcal./mole.

(C 3) Added tetra-*n*-butylammonium azide depresses the rate of the chloride exchange, and produces a side-reaction; but it depresses even the initial rate of exchange, thereby indicating a competition between the saline chloride and the saline azide for some slowly supplied intermediate. From the changes in the exchange rate it was deduced that the ratio of the specific rates of capture of the intermediate by the two saline competitors, both acting in ion-pair form, is close to unity.

(C 4) The rate of exchange is much increased by added nitro-compounds, which do not produce side-reactions; but the kinetic order of zero in salt is maintained. The initial rate is also much increased by added amines and by added hydroxy-compounds, which all produce side-reactions; but still the order of zero in salt, with respect to the initial rate, is maintained.

(C 5) The alcoholytic reactions, which accompany chloride exchange in the presence of hydroxy-compounds, are also accelerated by increasing the concentration of the latter, but not so sharply as is the exchange itself. Thus with [MeOH] < 0·01M, the methyl-alcoholysis rate, $0·35 \times 10^{-5}$ sec.$^{-1}$, is comparable to the exchange rate $0·32 \times 10^{-5}$ sec.$^{-1}$; but with [MeOH] = 0·10M, when both rates are much larger, the alcoholysis rate, $5·6 \times 10^{-5}$ sec.$^{-1}$, is already 8 times smaller than the exchange rate, 45×10^{-5} sec.$^{-1}$, at 25°. Similar effects are observed in exchange in the presence of benzyl alcohol. Thus with [C_7H_7·OH] = 0·02M, the rate of benzyl-alcoholysis is 6% of the rate of exchange, but with [C_7H_7·OH] = 0·05M, although both rates are considerably increased, the benzyl-alcoholysis rate is only 2·5% of the exchange rate. The same thing holds for the catalysis of exchange by phenol with accompanying phenolysis, though our experiments on this subject were only preliminary, and the figures obtained were not considered good enough to quote. But they do show that in exchange with [PhOH] = 0·001M, the rate of the accompanying phenolysis is about 5% of the exchange rate, whereas with [PhOH] = 0·005M, when both rates are much increased, the rate of phenolysis has fallen relatively to about 1% of the exchange rate. Always the hydroxylic catalyst, whilst it accelerates both reactions, discriminates against the reaction in which it stoicheiometrically participates.

(C 6) The exchange is not catalysed by tetra-*n*-butylammonium perchlorate, not even in the presence of methyl alcohol, when the salt appears to exert a mildly retarding influence.

The following are the main points which emerged from our study of the ***azide-substitution*** of triphenylmethyl chloride, with tetra-*n*-butylammonium azide as substituting agent (Part LV).

(A 1) At salt concentrations low enough to secure that nearly all the salt is present as ion-pairs, or as ion-pairs plus some quadrupoles, this substitution is of first order in triphenylmethyl chloride and of zeroth order in the saline azide.

(A 2) The specific rate of the azide substitution at 30° is $2{\cdot}5 \times 10^{-5}$ sec.$^{-1}$

(A 3) Tetra-*n*-butylammonium chloride, whether added or produced in the reaction, reduces the rate of the azide substitution, thereby indicating a competition between the two saline reagents for some slowly produced intermediate. From the changes in the rate of the azide substitutions, it was deduced that the ratio of the specific rates of capture of the intermediate by the saline competitors, both acting in ion-pair form, is close to unity.

(A 4) The azide substitution is catalysed by phenol, but the catalysed reaction has no particular kinetic order in phenol. This catalysis is comparable in strength to the analogous catalysis of chloride exchange. It is much stronger than the corresponding catalyses of methyl- and benzyl-alcoholyses.

(A 5) The azide substitution is not catalysed by tetra-*n*-butylammonium perchlorate.

We now extract such results as we shall need from our investigation of the *methyl-alcoholysis* of triphenylmethyl chloride in benzene (Part LVI).

(M 1) This reaction is of first order in triphenylmethyl chloride, but except at quite low concentrations of methyl alcohol, it is of inconstant order in methyl alcohol. In the range [MeOH] = 0·002—0·01M, the order in methyl alcohol is approximately zero; but in the range [MeOH] = 0·01—0·5M, the formal order rises continuously from near zero to about three.

(M 2) In the range over which the precise concentration of methyl alcohol is unimportant, [MeOH] = 0·002—0·01M, the specific rate of the methyl-alcoholysis is about $0{\cdot}35 \times 10^{-5}$ sec.$^{-1}$; at [MeOH] = 0·1M it is $5{\cdot}6 \times 10^{-5}$ sec.$^{-1}$, and at [MeOH] = 0·3M it is 137×10^{-5} sec.$^{-1}$, all these values applying to 25°.

(M 3) Added tetra-*n*-butylammonium chloride depresses the rate of methyl-alcoholysis. A minor part of the depression is due to the destruction of catalysis by the hydrogen chloride present in the experiments, but the important depression is of the uncatalysed rate. The functional form of this effect is in approximate agreement with the assumption that the salt in ion-pair form is competing with methyl alcohol for some slowly produced intermediate. From the rate depressions it was deduced that the specific rate of capture of the intermediate by the saline ion-pair is about 5 times as great as the specific rate of its capture by the methyl alcohol molecules, when methyl alcohol is 0·1M.

(M 4) The methyl-alcoholysis is catalysed by nitro-compounds, by phenol, and by hydrogen chloride. Only in the last case is the kinetic order in the catalyst integral and constant. The formal kinetic order in the catalyst rises markedly with the concentration of the nitro-catalysts, rises above unity in phenol, but remains unity in hydrogen chloride. There is also some qualitative evidence of catalysis by free (*i.e.*, solvated) protons.

(M 5) The methyl-alcoholysis is strongly catalysed by tetra-*n*-butylammonium perchlorate. Over the ranges of concentration in which the electrolytic situation can be considered simple, the catalysed reaction has a kinetic order of one-half in the salt. From this, and the quantitative specificity of the catalysis, it was concluded that the catalysing agent is the free perchlorate ion. The catalytic coefficient increases with the methyl alcohol concentration, but the catalysed reaction has not a constant kinetic order in methyl alcohol. The accelerating effect of methyl alcohol on the perchlorate-catalysed alcoholysis is proportionately weaker than its effect on the otherwise uncatalysed reaction.

(M 6) The catalysis by tetra-*n*-butylammonium perchlorate is strongly suppressed by added tetra-*n*-butylammonium chloride, and the functional form of the effect is in agreement with the assumption that the saline chloride as ion-pair is competing for some slowly formed intermediate, with those reagents which carry forward the catalysed reaction. The competing system must involve methyl alcohol, and there is some evidence that it involves the perchlorate ion.

Finally, we summarise the chief points emerging from our study of the *benzyl-alcoholysis* of triphenylmethyl chloride in benzene (Part LVII).

(B 1) The reaction is of first order in triphenylmethyl chloride, but of inconstant order in benzyl alcohol.

(B 2) As the concentration of benzyl alcohol is progressively reduced, both the absolute rate, and the degree of its dependence on the concentration of the alcohol, continuously diminish; and both were still diminishing at the lowest rate measured, which was $0{\cdot}37 \times 10^{-5}$ sec.$^{-1}$ at 30°. This must be an upper limit to the rate obtaining when the concentration of alcohol is low enough to be unimportant for the rate.

(B 3) Tetra-*n*-butylammonium chloride retards benzyl-alcoholysis, qualitatively as for methyl-alcoholysis (paragraph M 3).

(B 4) Nitro-compounds, phenol, and hydrogen chloride accelerate benzyl-alcoholysis, qualitatively as for methyl-alcoholysis (paragraph M 4).

(B 5) Tetra-*n*-butylammonium perchlorate strongly accelerates benzyl-alcoholysis, and, as far as was investigated, the kinetic pattern of the effect appeared to follow that described for methyl-alcoholysis (paragraph M 5).

(B 6) The catalysis of benzyl-alcoholysis by tetra-*n*-butylammonium perchlorate is very strongly suppressed by tetra-*n*-butylammonium chloride, and the functional form of this counter-catalysis is generally similar to that elucidated for methyl-alcoholysis (paragraph M 6).

(2) *Interpretation: Part* i. *Conclusions from Kinetics apart from Catalysis.*—The picture we shall build of S_N1-type substitutions in benzene, from the above observations, is inevitably more involved than the conventional picture applying to S_N1 reactions in ionophilic solvents. Partly for simplicity, and partly in order to make clear the reasons for the elaborations we shall introduce, we shall develop our interpretation in stages. For the first stage, we need consider only certain observations on the two substitutions by anions. These are the observations on substitution by chloride ion, noted in paragraphs C 1, C 2, and C 3, and those on substitution by azide ion, summarised in paragraphs A 1, A 2, and A 3, of Section 1.

Observation C 1 shows that the rate of substitution by chloride ion is unaffected by the (low) concentration of the saline chloride. The conventional conclusion would be that the measured rate is that of a reaction of some other material, but not of the saline chloride. The kinetic observation shows that the measured reaction is certainly a reaction of the triphenylmethyl chloride. Since this is the only other reagent, the measured reaction, so the argument goes, must be one of this alone. As an anion has finally to be brought into combination to form the product, a cation must somehow be provided; and hence the measured reaction is the ionisation of triphenylmethyl chloride.

In just the same way, observation A 1 shows that the rate of substitution by azide ion is unaffected by the (low) concentration of the saline azide. Again the usual conclusion would be that the reaction of which the rate is measured is not one of the saline azide, but is one of the triphenylmethyl chloride only, which becomes ionised.

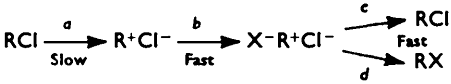
If we pursue this argument, it would seem hard to avoid the conclusion that the measured processes in these two substitutions are identical. But observations C 2 and A 2 show that they cannot be, because their rates are different.

We are therefore led to re-examine the logic of the standard kinetic argument; and when we do so, we see that it has a flaw. The logical conclusion to draw from our observation that a measured rate is independent of the concentration of a substance X is simply that the transition state of reaction is formed as easily in one concentration of X as in another. Any particularisation of this conclusion is not necessitated by the observation. The usual particularisation is that X is not present in the transition state. However. another possible particularisation is that X is present, but is so available that, at all practical concentrations, its accession never delays the formation of the transition state, which accordingly has nothing to gain from an increase in its concentration. To adopt the first alternative, without further evidence, as has not infrequently been done, is to jump to conclusions, and in our case to a difficult landing.

So let us consider the second alternative. We have triphenylmethyl chloride reacting, in separate experiments, with two reagents X and Y, at rates which, at practical concentrations, are independent of the concentrations of X and Y. But now X and Y are assumed to be ubiquitously present in the transition states. Then the two transition states are different, and so the rates can be different.

We shall now attempt to complement this abstract explanation by setting down some hypothetical chemical schemes which fulfil the conditions it indicates. We commence with a very simple scheme, which qualitatively does so, though we shall find that it is too simple to cover all the observations of which we have to take account.

Suppose that triphenylmethyl chloride RCl is slowly heterolysed to its ion-pair form R^+Cl^-, and that this then instantly attracts to itself the anion X^- of the saline reagent M^+X^- to form the triple ion $X^-R^+Cl^-$, which rapidly breaks down in the two possible ways, to form the factor RCl, and the product RX. We set down two such schemes, representing separate experiments, one with M^+X^- as the reagent, and the other with a second saline reagent M^+Y^- :



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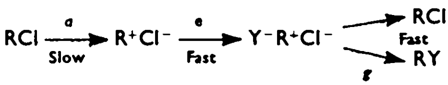

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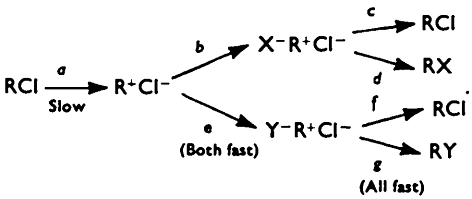
The labels "slow" and "fast" describe specific rates, whilst the small letters in the diagram represent instantaneous rates. Then, if no side-reactions occur, for the first experiment, $a = b = c + d$, and, for the second, $a = e = f + g$, at every instant. There will be a ratio $x = d/(c + d)$, which we can call the "yield" of the product RX from the triple ion which produces it. The rate of formation of RX in the first experiment is ax, and is specific to the substituting agent X^-, even though it does not depend on the concentration of M^+X^-, the only concentration on which it does depend being that of RCl. In the second experiment, the yield from the triple ion is $y = g/(f + g)$, and the rate of formation of RY is ay, which is a different rate, and specific to Y^-, though it does not depend on the concentration of M^+Y^-, but only on that of RCl.

We must now refer to the observations C 3 and A 3, which show that, despite the considerable difference in the rates of substitution by chloride ions and by azide ions in separate experiments, when the two substitutions are run together in a common solution, a given fraction of the faster-acting reagent does not proportionately reduce the rate of reaction with the slower-acting reagent by any more than the same fraction of the latter would reduce the rate of substitution by the former. To give a simple example, if the rate of substitution by the pure saline azide, in any concentration within limits, is 50 units, and the rate by the pure saline chloride is 10 units, then any concentration of an equimolar mixture of the two salts will lead to an azide substitution rate of 25, and concurrently a chloride substitution rate of 5 units. Thus the rate of total substitution, as well as the rates of its components, change with the composition of the saline reagent, though not with its concentration at a constant composition. But, even though the absolute rate-changes of the component substitutions are different, the fractional rate-changes, produced by a given fractional dilution of either salt by the other, are the same.

Our scheme allows us to expect a general competitive relation which is independent of the rate difference, and includes the relation described as a special case. This arises as follows. The rate of formation of RX in the separate experiment discussed above depends on the rate *a*, and on the rate-ratio *d*/*c*: it does not depend in any way on the kinetics of the reaction labelled *b*. And similarly, the rate of formation of RY in a separate experiment, depends on *a*, and on the ratio *g*/*f*, but not on the kinetics of the reaction labelled *e*. Now, setting down the scheme for the two reactions running concurrently in the same solution, as in (3) we have $a = b + e$, $b = c + d$, and $e = f + g$; and we see that the ratio in which R^+Cl^- enters the route that can lead to RX, and the route that can lead to RY, depends, not on the previously important rates, *a*, *c*, *d*, *f*, and *g*, but only on the ratio of the other two, previously immaterial rates, *b* and *e*. If the corresponding specific rates of these fast processes are *B* and *E*, so that $b = B[M^+X^-]$ and $e = E[M^+Y^-]$, then, when we measure the effect of added M^+Y^- on the rate of formation of RX, the intervention constant α_x^y will be E/B; and when we measure the effect of added M^+X^- on the rate of formation of RY, the intervention constant α_y^x will be B/E: each intervention (" mass-law ") constant is the simple reciprocal of the other, notwithstanding that the separate substitutions have different rates. The reagents tetra-*n*-butylammonium chloride and azide illustrate an approximation to a special case, inasmuch as both intervention constants were found to be approximately unity. This means that the specific rates of rapid attack by the two saline reagents on the common slowly formed intermediate are about equal ($B \approx E$). A possible reason for this will be suggested later (p. 1274). The point at present is that this approximate equality in competing power does not prevent the reagents from giving their products at quite different rates.



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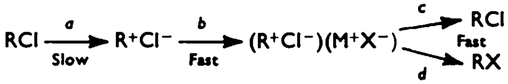
This first step in our interpretation of the kinetic data is so essential that we have chosen to illustrate it with an oversimplified scheme, which in the sequel has to be elaborated in more than one way. One elaboration may be introduced immediately, without looking beyond the limited group of observations on which we are at present concentrating.

The maximum value of a "yield," as we have defined it, is unity. Consider the special case $X^- = {}^*Cl^-$, this $^*Cl^-$ being isotopically labelled, to distinguish it from the chloride ion Cl^- derived from the triphenylmethyl chloride. The triple ion is then symmetrical, except for an isotopic difference, and so $c = d$, and the yield is one-half. Therefore our scheme does not allow a non-isotopic substitution to go at more than twice the rate of the isotopic substitution. But the azide substitution goes at 5 times the rate of the chloride exchange.

Symmetry must therefore be taken out of the relation between the anions and the carbonium ion in the product of the first rapid reaction-step. This product therefore cannot be simpler than a quadrupole, in which each anion occupies a position reflecting its origin:



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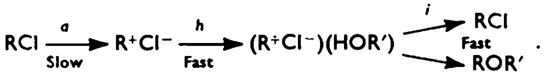
The reason why we write the quadrupole in a linear, rather than a cyclic form, is mentioned below (p. 1276).

Our reaction scheme is still a skeleton, but, as such, it can accommodate the observations from which we developed it. It can similarly accommodate six corresponding observations on alcoholysis, *viz.*, those summarised in paragraphs M 1, M 2, M 3, B 1, B 2, and B 3, of Section 1. For what the reagent saline dipole is assumed to do, the reagent molecular dipole should be able to do, even if not quite so quickly. The corresponding scheme for alcoholysis with an alcohol R'OH may be written



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the " yield " being $z = j/(i + j)$, and the measured rate az.

We know that rate of alcoholysis can approach independence of the alcohol concentration at sufficiently low concentrations, although at higher concentrations a catalytic effect comes in, which can be paralleled by catalysts other than the substituting agent. However, even when the rate does not depend on the reagent concentration, it still depends on the reagent. It is true that the limiting rate of methyl-alcoholysis is nearly the same as that of chloride exchange, but a survey of the rates assembled in Table 1 shows that this particular near-equality is only a coincidence : the rate of benzyl-alcoholysis is smaller, and that of azide substitution larger.

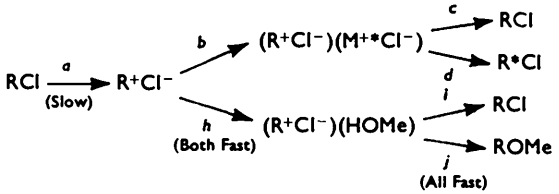
TABLE 1. *Comparison of specific rates of substitution of triphenylmethyl chloride in benzene, when rate depends on the concentration of triphenylmethyl chloride, but not on the concentration of the substituting agent.*

($M^+ = Bu^n{}_4N^+$; k_1 in sec.$^{-1}$.)

Substituting agent	M^+Cl^-	$M^+N_3^-$	$CH_3{\cdot}OH$	$C_7H_7{\cdot}OH$
10^5k_1 at 25°	0·32	—	0·35	—
,, 30°	0·50	2·5	—	<0·37

In the interpretation represented by our scheme, the yield $j/(i + j)$ in methyl-alcoholysis is nearly the same as the yield $d/(c + d)$ in chlorine exchange, provided that the reagent concentrations are low enough. But when the concentration of methyl alcohol is sufficiently large to make it a significant constituent of the solvent, then, not only are both reactions accelerated, but also they are accelerated unequally, and so, in terms of our interpretation, the yields must become unequal. In 0·1M-methyl alcohol, for example, $d/(c + d)$ is 8 times larger than $j/(i + j)$. A possible reason for this will be suggested later (p. 1272).

When the two substitutions are run together in competition so that $a = b + h$, then the rates, b and h, of the fast steps in which the substituting agents enter reaction, and also their specific rates, B and H, given by $b = B[M^{+*}Cl^-]$ and $h = H[MeOH]$, are not the same :



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For the conditions in which we determined it, the specific rate of capture of the saline ion-pair was about 5 times larger than that of the molecular reagent : $B/H \approx 5$. Whether this ratio is subject to a co-solvent effect of methyl alcohol, is a question that we have still to settle.

(3) *Interpretation : Part* ii. *Conclusions from Kinetics including Catalysis.*—So far we have taken account of only 12 of the 23 observations listed in Section 1. It

is now necessary to consider the remainder, and we shall discuss first a set of 5, *viz.*, those summarised in paragraphs C 4, A 4, M 4, B 4, and C 5.

The first four of these show that all the substitutions are catalysed by various non-ionic but polar molecules. This is true for the anion substitutions, and for the alcoholyses; and in the latter case it remains true when the molecular catalyst happens also to be the substituting agent.

Observation C 5 relates to hydroxy-compounds as catalysts, and particularly to their comparative effects on rate of chloride exchange, and on the ether-forming reactions which accompany exchange in their presence. These catalysts, methyl alcohol, benzyl alcohol, and phenol, always accelerate the chloride exchange more than they accelerate the alcoholytic or phenolytic reaction in which they stoicheiometrically participate.

By comparing rates among the experiments to which paragraphs C 4, A 4, M 4, and B 4 refer, we find that catalysis by polar molecules is generally more marked in the anion substitutions than it is in the alcoholyses. Catalysis by phenol provides a convenient illustration, since this was investigated for all the four reactions studied. 0·05M-Phenol increased the rate of chloride exchange 115 times, that of the azide substitutions 175 times, of methyl-alcoholysis 18 times, and of benzyl-alcoholysis 13 times: the factors of acceleration fall into two orders of magnitude.

Our reaction scheme in its present state of development explicitly shows the ionisation of triphenylmethyl chloride as the one rate-controlling step of all these reactions. Certainly its transition state must be much more polar than its initial state. Indeed, it follows from the general weakness of ion-solvation by benzene, that the transition state of an ionisation in this solvent must resemble the fully formed ion-pair, much more closely than it resembles the initial molecule. Therefore all polar molecules must strongly catalyse the ionisation, by virtue of the much greater interaction of their coulombic fields with the highly polar transition state than with the weakly polar initial molecule.

However, it may be questioned whether this is a complete description of the catalyses that we observe. For consider the catalysis by methyl alcohol of concurrent chloride exchange and methyl-alcoholysis, and particularly the catalytic discrimination against alcoholysis. Despite the great range of coulombic fields in benzene (Part LIII, Section 3), electrostatic catalysis does imply a certain concentration of the catalysing molecules towards the transition state. We should expect that such temporary concentrations of methyl alcohol molecules would increase their local availability, and so would heighten the chance of capture of a newly formed ion-pair of triphenylmethyl chloride by a methyl alcohol molecule, relatively to the chance of its capture by a saline radiochloride ion-pair. The conclusion, deriving from the experimental data, that catalytic acceleration by methyl alcohol diverts the reaction away from the route involving methyl alcohol, makes no sense on this picture. Here we have an indication that the first step of the reaction may not be the exclusive rate-controlling step, and that perhaps rate is determined by some form of joint control.

Thus we may arrive at the idea that all these substitutions may have a second rate-controlling step. We can already assign to it some necessary properties. The immediate precursor of the assumed second rate-controlling step in methyl-alcoholysis must already contain the methyl alcohol molecule which is to react, in order that the reacting system shall not be dependent on acquiring one of those ambient molecules of methyl alcohol, whose local concentration we change when we investigate catalysis by methyl alcohol. Presumably an analogous inclusion of the substituting agent will have occurred in the same stage of the other substitutions. This is consistent with the generally stronger catalysis by polar molecules of anion exchange than of alcoholysis, a difference which must mean that the transition state of the second and final rate-controlling step of the anion substitution has a more inhomogeneous coulombic field, and therefore a field which interacts more strongly with the ambient dipoles than does the field of the transition state of the corresponding step of alcoholysis. This is intelligible if the place of the alcohol molecule in alcoholysis is being taken by the saline dipole, with its two fully formed ions, in the immediate precursor of the final transition state of the anion substitution.

We reach similar conclusions, if we consider the remaining set of 6 observations, *viz.*, those applying to catalysis by salts, especially tetra-*n*-butylammonium perchlorate, as described in paragraphs M 5, B 5, C 6, A 5, M 6, and B 6, of Section 1.

Observations M 5 and B 5 show that the catalysis of alcoholysis by this salt is very strong, and is of such kinetic form that the active agent may be concluded to be the free perchlorate ion. The catalysis is so strong, expecially considering that the attainable concentrations of this anion are only of the order 10^{-10}—10^{-9}M, that we must regard it as involving a drastic short-circuiting of some rate-controlling step.

However, observations C 6 and A 5 show that the reactions of anion substitution are not similarly catalysed by perchlorate. Therefore it is not possible to identify the step which is being by-passed, with a step which is common to all the substitutions, alike by molecular reagents and by anions. Also, if perchlorate ion could catalyse the initial ionisation, the chloride ion and the azide ion should be able similarly to intervene in this step, and that would produce bimolecular chloride exchange, and bimolecular azide substitution for which reactions we could find no evidence (paragraphs C 1 and A 1 of Section 1).

Furthermore, observations M 6 and B 6 show that the catalysis of alcoholysis is very strongly repressed by tetra-*n*-butylammonium chloride, and that the functional form of this counter-catalysis points to a competitive intervention by the suppressing agent in a fast process for some slowly formed intermediate. The active counter-catalytic agent is almost certainly the tetra-*n*-butylammonium chloride ion-pair. There is qualitative evidence that what it competes against is a combination involving both the alcohol and the perchlorate ion, though we have still to prove this quantitatively. The position thus appears to be that the perchlorate ion is intervening after a slow step, and yet it is by-passing a slow step; and that it can itself be by-passed by the product-determining step of an anion substitution, which it does not catalyse. So again we arrive at the picture of two rate-controlling steps, with a fast product-determining step, in which the substituting agent is fully captured, interposed between them.

Now this idea is really contained in the reaction schemes already written, even though they do not show it, provided that we accept the principle of microscopic reversibility at least in its application to sufficiently slow processes. Consider, for example, scheme (4) (p. 1270), with X specialised to *Cl, the asterisk signifying an isotopic distinction. The quadrupole appearing in the scheme, in our special case $(R^+Cl^-)(M^{+*}Cl^-)$, has a fast route, labelled *c*, by which it can revert to RCl. But there can be no faster route of reversion than the retracing of the steps, labelled *a* and *b*, by which the quadrupole was formed from RCl. Now it will be recalled that we had to keep anion-symmetry out of the quadrupole, in order that the yield, $d/(c + d)$, in chloride exchange could be less than one-half; for our rate comparisons indicated that it was indeed less. In other words, we had so to shape the scheme that process *d* would be somewhat slow compared with process *c*. In our special case, the product of process *d* is R*Cl. Now consider process *d* in reverse. The fastest route back from R*Cl to the quadrupole $(R^+Cl^-)(M^{+*}Cl^-)$ must consist simply in a retracing of route *d*. But since R*Cl has exactly the same chemical properties as RCl, this retracing must start with two steps like *a* and *b*, and so must lead first to a stereoisomeric quadrupole $(R^{+*}Cl^-)(M^+Cl^-)$. To complete the backward process, we have to interconvert the two quadrupoles, and that is a step which must obviously pass through a transition state with anion-symmetry, and have the same rate in both directions. This step, therefore, has to be introduced also into the forward process *d*; and it is the only step which could make process *d* slower than process *c*. It is implied that the isomerisation of quadrupoles is an activated process. Its energy of activation can only be electrostatic, but we shall see presently that the required energy could be quite sufficient.

This argument, based on the principle of microscopic reversibility, is most simply set down for the case of isotopic substitution. We could develop arguments, which are inevitably longer, but have the same end result, for all the substitutions: in all of them, the second slow step is a quadrupole rearrangement. In anion substitutions, its activation energy is wholly electrostatic. In the substitutions by non-ionic reagents, the activation energy is partly covalent and partly electrostatic. The transition states will involve a similar disposition of the two anions or potential anions, with respect to the carbonium ion. Thus in anion substitution, the transition state of the quadrupole rearrangement can, as one possibility, be regarded as a carbonium ion centred against a saline triple anion. In the alcoholytic substitutions, it can be considered as a carbonium ion similarly associated with a hydrogen-bonded, and hence semi-electrovalent, complex anion $(\mathrm{Cl}\cdots\cdots\mathrm{H}\cdots\cdots\mathrm{OR'})^-$.

In accordance with these considerations, we may now rewrite scheme 4, and similarly schemes 5 and 6 (the last with some generalisation), in the fully explicit forms 7, 8, and 9, respectively.* For the steps of the forward reactions, we retain the previous letter-labels as far as applicable, and introduce some new ones for the quadrupole rearrangements:

$$\mathrm{RCl} \xrightleftharpoons[\text{Fast}]{(a)\ \text{Slow}} \mathrm{R^+Cl^-} \xrightleftharpoons[\text{Fast}]{(b)\ \text{Fast}} \left\{\begin{matrix}\mathrm{R^+Cl^-}\\ \mathrm{M^+X^-}\end{matrix}\right\} \xrightleftharpoons[\text{Slow}]{(k)\ \text{Slow}} \left\{\begin{matrix}\mathrm{R^+X^-}\\ \mathrm{M^+Cl^-}\end{matrix}\right\} \xrightleftharpoons[\text{Fast}]{\text{Fast}} \mathrm{R^+Cl^-} \xrightleftharpoons[\text{Slow}]{\text{Fast}} \mathrm{RX} \quad . \quad . \quad . \quad (7)$$

$$\mathrm{RCl} \xrightleftharpoons[\text{Fast}]{(a)\ \text{Slow}} \mathrm{R^+Cl^-} \xrightleftharpoons[\text{Fast}]{(h)\ \text{Fast}} \left\{\begin{matrix}\mathrm{R^+Cl^-}\\ \mathrm{HOR'}\end{matrix}\right\} \xrightleftharpoons[\text{Slow}]{(i)\ \text{Slow}} \left\{\begin{matrix}\mathrm{R^+OR'^-}\\ \mathrm{HCl}\end{matrix}\right\} \xrightleftharpoons[\text{Fast}]{\text{Fast}} \mathrm{R^+OR^-} \xrightleftharpoons[\text{Slow}]{\text{Fast}} \mathrm{ROR'} \quad . \quad . \quad (8)$$

$$\begin{tikzcd}
 & & \left\{\begin{matrix}\mathrm{R^+Cl^-}\\ \mathrm{M^+X^-}\end{matrix}\right\} \arrow[r, shift left, "(k)"] & \left\{\begin{matrix}\mathrm{R^+X^-}\\ \mathrm{M^+Cl^-}\end{matrix}\right\} \arrow[l, shift left] \arrow[r, shift left] & \mathrm{R^+X^-} \arrow[l, shift left] \arrow[r, shift left, "\text{Fast}"] & \mathrm{RX} \arrow[l, shift left, "\text{Slow}"] & \\
\mathrm{RCl} \arrow[r, shift left, "(a)\ \text{Slow}"] & \mathrm{R^+Cl^-} \arrow[l, shift left, "\text{Fast}"] \arrow[ur, shift left, "(b)"] \arrow[dr, shift left] & & & & & \cdot\ (9) \\
 & & \left\{\begin{matrix}\mathrm{R^+Cl^-}\\ \mathrm{HOR'}\end{matrix}\right\} \arrow[ul, shift left, "(h)\ \text{All fast}"] \arrow[r, shift left, "(l)"] & \left\{\begin{matrix}\mathrm{R^+OR'^-}\\ \mathrm{HCl}\end{matrix}\right\} \arrow[l, shift left, "\text{All fast}"] \arrow[r, shift left] & \mathrm{R^+OR'^-} \arrow[l, shift left, "\text{All fast}"] \arrow[r, shift left, "\text{Fast}"] & \mathrm{ROR'} \arrow[l, shift left, "\text{Slow}"] &
\end{tikzcd}$$

It will be obvious that the results considered in Section 2 can be accommodated by these expanded schemes. In particular, substitution rate can depend on the nature, but not on the concentration, of the substituting agent; the rate of a substitution can not only be smaller than the isotopic exchange rate, but can also be greater, in particular greater than twice that rate; yet the substitutions show, in a completely normal way, the competitive effects characteristic of S_N1 reactions.

Even the apparently coincidental result, that tetra-*n*-butylammonium chloride and azide, though they substitute at quite different rates, have almost identical competing effciencies, seems rational. For competing efficiency depends on the first fast step (*b*) of each of these substitutions. The driving force in this step is electrostatic, a dipole–dipole attraction of fairly long range, which should be nearly identical as between the alkyl halide ion-pair and two saline ion-pairs of similar dipole moment.† The important resisting forces in this fast process are probably those of viscous transport, and their main determinant will be the electrokinetic mobility of the large tetra-*n*-butylammonium ion, which is the same for both salts. Thus the competing efficiencies of the two salts should be very similar.‡ The difference in their rates of reaction depends, not on the fast step (*b*), but on the slow succeeding step (*k*); and this is a matter of detailed local geometry, and of short-range forces, which will be considerably different for the two substitutions.

There is no difficulty in understanding on these lines the result that the competing efficiency of the alcohols is smaller than that of the salts, even though the rate of reaction

* Perhaps in schemes 8 and 9, $\mathrm{R^+OR'^-}$ and ROR′ should be rewritten with inclusion of a proton in each case.

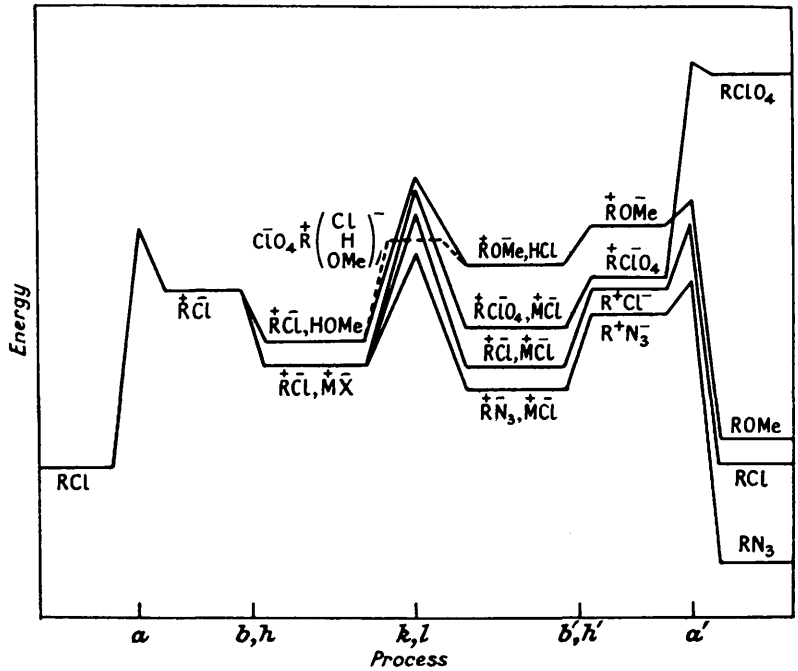
† We infer the similarity of the saline dipole moments from the practically identical ion-pair parameters a_1 of our salts, and from Fuoss and Kraus's direct measurements of the dipole moments of some similar salts in benzene (cf. Part LIII, Table 1, and ref. 7). We have not yet directly measured the dipole moments of our salts, but intend to do so.

‡ Dipole association will normally be complete in less than 10^{-8} sec.

of an alcohol is not necessarily smaller than that of a salt, as has been illustrated for methyl-alcoholysis in comparison with chloride exchange.

It will facilitate the further discussion of catalysis to think of schemes (7), (8), and (9) qualitatively in terms of the energy changes they imply. The overall energy of activation is the endothermicity of the ionisation, (*a*), minus the exothermicity of the dipole association, (*b*) or (*h*), plus the energy of activation of the quadrupole rearrangement, (*k*) or (*l*). For ease of back-translation to reaction rates, we can consider entropy terms as always included, so that all our energies are really free-energies. For each substitution, we can take the energy of the initial state as the arbitrary zero, so that for all substitutions

Schematic energy-configuration curves, representing the theory of joint rate-control by ionisation and quadrupole rearrangement, with intervening product-control by dipole association, in S_N1 *substitutions in a weakly solvating solvent* ($X^- = Cl^-, N_3^-$, or ClO_4^-).



it is the same, and we have not to think about the energy of the substituting agent until it becomes associated with the substrate. The energy scale is also arbitrary to the extent that, if we draw an energy curve for a particular substitution under given conditions, and then proceed to use it in a discussion of catalysis, we must regard the levels and summits as shifted downwards in energy, some more than others, by the addition of a catalyst, or by an increase in the concentration of a substituting agent which acts also as a catalyst. These are the conventions on which the schematic diagram of the Figure has been constructed, in which we have introduced the further simplification of assuming that the energies of association of the common substrate ion-pair, R^+Cl^-, with the three saline ion-pairs M^+Cl^-, $M^+N_3^-$, and $M^+ClO_4^-$, collectively symbolised M^+X^-, are the same. We do this because the competition experiments indicated that it is approximately true for M^+Cl^- and $M^+N_3^-$, though we cannot verify it for $M^+ClO_4^-$, because the high energy (*i.e.*, the practical non-existence) of covalent $RClO_4$ prevents this reagent from yielding a product. And so in the diagram the curves for the three salts do not spread out before the stage of quadrupole rearrangement. Again for simplicity, the labels attached to the energy levels express only what is associated with triphenylmethyl R; but the energies of the reagent or eliminant must be understood to be included.

We may here indicate why we think quadrupole rearrangement can provide a significant contribution to the energetics The basic reason is that a very substantial fraction of the total work of separating any two fairly small ions in a weakly solvating solvent is done in the first Ångstrom of separation, and temporary charge separations of that order are involved in rearrangements.

We cannot, of course, attempt anything more than an order-of-magnitude calculation, but for this purpose the following rough models will serve. For the tetra-*n*-butylammonium ion, we take a sphere of averaged radius 4 Å: such spheres would pack to a reasonable liquid density if the net charge were taken out. For either anion, we assume a sphere of radius 2 Å, which is approximately right for a chloride ion. For the triphenylmethyl carbonium ion, when free, or in symmetrical immediate surroundings, we take a cylinder, of average van der Waals radius 5 Å, and effective thickness 5 Å, dimensions which give a reasonable packing density, the thickness allowing for the necessarily large twisting of the phenyl groups; and we take the charge as central, though it must actually be spread over the volume of the ion. When this cation is associated with a single anion, it probably goes into a mildly pyramidal form, with the charge rather well localised on the central atom. We represent this form of the cation by replacing the faces of the former cylinder by a projecting and a re-entrant blunt cone, each of height 1 Å, representing a bond-bending angle near 10°, *i.e.*, a degree of bending about half-way towards tetrahedral bending; and now we assume the charge to be only 1·5 Å behind the projecting apex, in order that the charge separation in an ion-pair shall be nearly what it would be in a corresponding aliphatic ion-pair.

With these models, we can conveniently work at first in units $10^8e^2/D$, where e is the electronic charge, and D the effective dielectric constant: energy terms are then given directly by the reciprocals of charge separations in Ångstroms. The total energy of the ion-pairs M^+Cl^- and R^+Cl^-, when widely separated, is $-0{\cdot}453 + \varepsilon$ units, where ε is the bending energy of the carbonium ion, and the energy zero is the energy with all ions widely separated.

In general, dipoles may associate either laterally or longitudinally, lower energies being attained by lateral association if the dipoles are long and thin, and by longitudinal association if they are short and thick. In our case, the most stable quadrupoles arise by longitudinal association. There are two possible linear quadrupoles. One of them is of the form $(M^+Cl^-)\,(R^+Cl^-)$, and presumably contains the flat form of R^+; its energy is $-0{\cdot}472$ unit. The other is of the form $(R^+Cl^-)\,(M^+Cl^-)$; and, if we assume that it contains the mildly pyramidal form of R^+, its energy will be $-0{\cdot}495 + \varepsilon$ units. This is probably the more stable form of the quadrupole, since ε is a somewhat small energy quantity.

There are two possible types of symmetrical transition state. In one, which we symbolise $R^+(Cl^-M^+Cl^-)$, the triple anion spreads itself across the flat, or the obtusely conical, face of the carbonium-ion model. If we assume the flat model, the energy of this transition state is $-0{\cdot}366$ unit. If we take the conical model, the energy is $-0{\cdot}391 + \varepsilon$ units. The latter form is probably the more stable. In the other type of transition state, which we may symbolise $M^+(Cl^-R^+Cl^-)$, the ammonium ion M^+ occupies the median plane of the flat carbonium ion, while the chloride ions occupy symmetrical positions near the centre of the carbonium ion. The energy of this state is $-0{\cdot}422$ unit; and so this is the most stable of the transition states considered. It does not become still more stable when the Cl^- ions are moved in parallel away from the R^+ centre towards M^+.

Considering now only the most stable of the quadrupoles and transition states, we find that the exothermicity of quadrupole formation is 0·042 unit, and that the activation energy of quadrupole rearrangement is $0{\cdot}073 - \varepsilon$ units. We cannot compute the bending energy ε, but it is probably small enough to be neglected in so rough a calculation. If we assume this energy to be $\frac{3}{2}\Gamma\theta^2$, where Γ is the bending moment-constant, and θ is the angle through which each carbonium-ion bond is bent out of its original plane, then with $\Gamma = 10^{-12}$ dyne-cm./radian, the bending energy comes to 0·8 kcal./mole. Our energy values are much more seriously affected by what we take for the effective dielectric constant D. Obviously we have not to take orientation polarisation into account, but only electron polarisation, whether of the reacting species or of benzene; and since the refractive indices of so many compounds of octet structures are near 1·5, it should be fairly satisfactory to take the square of this, 2·25, which also happens to be the dielectric constant of benzene. With this value of D, our energy unit is equal to 148 kcal./mole; and so the exothermicity of quadrupole formation is 6 kcal./mole, and the activation energy of quadrupole rearrangement is $10{\cdot}8 - \varepsilon$, or, say, 10 kcal./mole.

The experimental activation energy for chloride exchange is 16 kcal./mole (Section 1, paragraph C 2). . If we should accept the figures derived by calculation, the heat of ionisation of the triphenylmethyl chloride in benzene would become $16 - 10 + 6 = 12$ kcal./mole. We cannot calculate the separate activation energies of ionisation, and of covalent formation from ions, of triphenylmethyl chloride, but the latter must be much smaller than the former, and so smaller than 12 kcal./mole. It may possibly be almost zero. According as it is, or is not, smaller than 4 kcal./mole, the overall activation energy will, or will not, be greater than the activation energy of the primary ionisation. We are not so much concerned here with actual values as with showing by a calculation based on models, that, in a solvent such as benzene, primary ionisation will be succeeded by a number of electrostatic processes of ionic regrouping, each of such energetic importance that their sum can quite well determine a kinetically significant difference between the activation energy of the primary ionisation and the overall activation energy, and therefore between rate of ionisation and overall rate. Needless to say, quadrupole formation and rearrangement might lead to an entropic rate factor of some importance, but our present models are too crude to allow us theoretically to investigate this possibility.

Hudson and Saville's remark[1] that reactions similar to those here studied might pursue mechanisms intermediate between the mechanisms S_N1 and S_N2C^+, suggests another possible approach to modified S_N1 mechanisms, such as that now described.*

We return now to the subject of catalysis. As to catalysis by polar molecules, a catalysis common to all the substitutions, the most important things have been said, but the Figure will perhaps make it clearer that such catalysis is a composite phenomenon. Ambient dipoles will statistically dispose themselves about every polar configuration of reactants in such a way as to reduce its energy. They will thus lower the activation energy of the preliminary ionisation; and partly on this common account, but partly also on account of their effect, by the same electrostatic mechanism, on the exothermicity of dipole association, and on the activation energy of quadrupole rearrangement, they reduce the overall activation energy. Because each of the last two contributions to the total effect will change from one substitution to another, the overall reduction of activation energy will be different for the different substitutions. We have already ascribed the stronger catalysis by polar molecules of anion substitution than of alcoholysis to the more polar character of the rearranging quadrupole in anion substitutions. In the Figure, the curves for chloride exchange and methyl-alcoholysis are drawn as though such catalysis had already reduced the activation energy of the former reaction below that of the latter.

A more specialised problem is presented by the catalytic action of salts, in particular, of tetra-*n*-butylammonium perchlorate. This catalysis is specific for alcoholysis, and does not apply to anion exchanges. The kinetic effect followed the square-root of the salt concentration, and it was accordingly concluded in Part LVI that the active agent is the simple perchlorate ion (there being obvious reasons why it was not the tetra-*n*-butyl-

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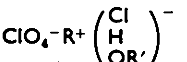
* As to S_N2C^+ reactions, cf. Gelles, Hughes, and Ingold, *J.*, 1954, 2918. Some interesting new examples, though they are not so labelled, have been given by Bethell and Gold (*Chem. and Ind.*, 1956, 741).

[1] Hudson and Saville, *J.*, 1955, 4138.

ammonium ion). Earlier in this Section, we concluded that this anion intervenes between the two slow steps, and that it replaces the transition state of the second by some markedly different transition state.*

The general reason for the selectivity of this catalysis seems fairly clear. If the perchlorate ion were to attack the first-formed quadrupole in chloride exchange, or in azide substitution, its most probable action would be to displace the saline anion, thereby giving an energetically nearly equivalent quadrupole (R^+Cl^-) $(M^+ClO_4^-)$, which cannot give a reaction product. Therefore the perchlorate ion does not catalyse. In a pure benzene solvent, there is never enough of it to render noticeable a retarding action, due to temporary sheltering of R^+Cl^- in the perchlorate quadrupoles. With the larger concentrations that can be introduced into benzene containing methyl alcohol, we may have observed a depression, by added perchlorate, of the initial rate of chloride exchange; but it is difficult to be sure, because, as explained in Part LIV, there is, in these circumstances, a progressive apparent retardation, due to a radioactive dilution of the original radiochloride, in consequence of the concurrent alcoholysis.

When the perchlorate ion attacks the corresponding alcoholytic quadrupole, the only anion it can displace is that derived from the original triphenylmethyl chloride; and this is a much more complex process. A half-way stage in it might be depicted as a triple ion, (*A*) with a hydrogen-bonded anionic component. This will proceed to lose HCl, and then can lead only to the product ROR′. These may be metastable configurations on the way to the configuration represented, which itself might be a transition state, or might have metastability. The critical part of the catalysed process of methyl-alcoholysis is represented in the Figure by a broken line, as a signal that we have now changed our energy zero in a new way, by including everywhere the energy of the perchlorate ion, which is not stoicheiometrically a reactant. But with this convention, the energy of the hydrogen-bonded triple ion must lie lower in the diagram than that of the half-rearranged quadrupole for alcoholysis without perchlorate.



$$ClO_4^-R^+\left(\begin{matrix}Cl\\H\\OR'\end{matrix}\right)^-$$

(*A*)

We can understand the observation that the superposed catalytic effect of methyl alcohol on the perchlorate-catalysed alcoholysis is weaker that the catalytic effect of methyl alcohol on the otherwise uncatalysed alcoholysis. For the perchlorate-catalysed reaction has, in its initial state, a free perchlorate ion, which must lose some of its external field when it becomes bound in the transition state.

An added saline chloride must be assumed to turn perchlorate out of the complex triple ion, and so determine reversion to the quadrupole $(R^+Cl^-)(HOMe)$, or, if enough chloride is added, to the quadrupole $(R^+Cl^-)(M^+Cl^-)$; so that, according to the quantity employed, we return to the unaccelerated, or to a retarded, alcoholysis. The sensitiveness

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* Winstein and his co-workers (Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2763, 2769, 2780; Fainberg, Winstein, and Robinson, *ibid.*, p. 2777; Winstein and Clippenger, *ibid.*, p. 2784) have described what they call a "special" accelerative effect of low concentrations of lithium perchlorate on the solvolysis of certain alkyl sulphonates in acetic acid. As far as we can see from the figures given, this acceleration is not so far from proportionality to the square-root of the salt concentrations that one should not consider assigning it to the simple perchlorate ion of the slightly ionised salt. At higher concentrations of salt, a linear acceleration sets in, which it would seem reasonable to ascribe to saline ion-pairs. The authors seem not to have considered that the two accelerations might arise from different saline species. They emphasize strongly, to the point of illustrating (twice) that a displayed linear relation, when replotted semilogarithmically, gives a curve, that they never find a linear dependence of the logarithm of the rate on the salt concentration, a form of relation which we deduced some time ago from ion-atmosphere theory, and illustrated by solvolysis in aqueous acetone (Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979). Here they forget that ion-atmosphere theory would be inapplicable to the salts employed in solvent acetic acid (as in some other solvents they mention), in which, at the concentrations of the measurements, lithium perchlorate, for example, would exist almost entirely as ion-pairs, in equilibrium with relatively few simple ions. Thus the ion-pair concentration would be nearly equal to the salt concentration, whilst the free-ion concentration would be proportional to the square-root of the salt concentration. In regard to range of penetration by Coulombic forces, acetic acid, of dielectric constant 6·2, is a very weakly polar solvent, probably because most of its molecules are cyclic dimers of zero dipole moment. The kinetics of S_N1 reactions in acetic acid might therefore have some features in common with their kinetics in benzene, including the possibility of involvement of the substituting agent after ionisation, but before rate is fully determined.

of the counter-catalysis, can be ascribed to the low concentration of available perchlorate ion, and to the energy differences between the complex triple ion and the quadrupoles.

This concludes our comparative discussion of the observations in the preceding papers. The group of observations as a whole presents many features which have little precedent, and it would be too much to hope that our attempts to include them in a self-consistent interpretation is correct in all particulars. However, the general idea than an S_N1 reaction in a weakly solvating solvent may involve more than one stage of rate-control, with intervening product-control, seems to cover the facts so far established. It is a concept that we shall certainly try to test further.

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