Mechanism of Substitution at a Saturated Carbon Atom. Part XXXVI.*
Unimolecular Menschutkin Reactions in Sulphur Dioxide Solution.
Remarks on the Theory of Border-line Mechanisms.

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As sequel to a previous investigation on the kinetics of nucleophilic aliphatic substitution by fluoride ion in *m*-chlorobenzhydryl chloride, with sulphur dioxide as solvent, the kinetics of the reactions of pyridine and triethylamine with that alkyl halide have been investigated in the same conditions. These reactions, like the fluoride-ion reaction, are essentially unimolecular, showing strong mass-law retardations; but, unlike the fluoride-ion reaction, the amine reactions show significant quantitative deviations from the strict requirements of the unimolecular mechanism. The nature of the deviations is such as to suggest that the use of the amines as substituting agents has introduced a tendency towards the bimolecular mechanism. Yet the results cannot be understood on the basis that, while most of the individual molecular acts of substitution pursue the unimolecular mechanism, some of them concurrently follow the bimolecular. The data are, however, not inconsistent with a qualitative picture of what might be expected if, in the beginnings of a general change from a unimolecular to a bimolecular mechanism, the individual molecular acts of substitution took on characters intermediate to various degrees between the two extremes.

MOST of our previous work on unimolecular nucleophilic substitution has related to reactions in hydroxylic solvents, whose polar groups are outstanding in the strength of their attraction for ions. The conclusions reached have been summarised in a mechanistic picture of the formation and reactions of the carbonium ion in such solvents (Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979). The other class of solvents that might conceivably support some form of unimolecular substitution, even though such solvents are, on the whole, less solvating than are hydroxylic solvents, are the polar aprotic solvents, such as sulphur dioxide, nitromethane, and acetonitrile, that is, solvents having large dipoles in small molecules, but no exposed protons. Work on nucleophilic substitution in solvents of this class was begun with solvent sulphur dioxide during the late 1930's, was then interrupted, but has since been resumed, while parallel studies with other solvents of the class have been commenced.

The work of the 1930's relating to solvent sulphur dioxide (Bateman, Hughes, and Ingold, *J.*, 1940, 1011, 1017) is reviewed here so as to give the observational and interpretative background of the developments reported in the present three papers. First, a semi-quantitative survey was made of initial rates of substitution in benzhydryl chloride,†
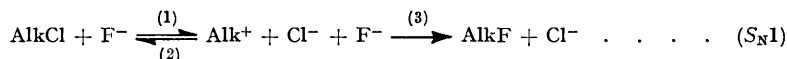
* Part XXXV, *J.*, 1952, 2499.
† The long-established name, benzhydryl chloride, is convenient for discussions such as the present one, particularly when these involve also substituted derivatives. The systematic names, based on diphenylmethyl chloride and recommended by I.U.P.A.C., will be used for description of individual compounds. ED.

and in *m*-chlorobenzhydryl chloride, using a variety of substituting agents—fluoride ion, iodide ion, pyridine, triethylamine, and water. At this stage, no attempt was made to define the somewhat complex kinetic forms of the reactions, or to correct measured rates to conditions of ideality. The object was to discover whether the rates differed widely, as would be expected if the substitutions were bimolecular, or whether the rates with different substituting agents were identical to within a range of deviations conceivably due to non-ideality, as should be the case if the substitutions were all unimolecular and rate-controlled by the same ionisation. It was found that the rates with different substituting agents, although not identical, were all of the same order of magnitude, a result which told somewhat strongly against the bimolecular mechanism, whilst it allowed, without providing a quantitative test for, a unimolecular interpretation.

The next task was to elucidate the kinetic forms of some of the substitutions, not only because this itself should shed light on mechanism, but also in order that idealised rates could be computed and the test of identity of unimolecular rates applied quantitatively. The second of the previous papers reported a detailed study of the kinetics of one such reaction, *viz.*, the substitution of *m*-chlorobenzhydryl chloride by fluoride ions, supplied as tetramethylammonium fluoride, in sulphur dioxide solvent at $-10.75°$.

This reaction had no simple kinetic order, but showed three striking kinetic features. With raised initial concentrations of tetramethylammonium fluoride, it started more rapidly, though not nearly to the extent of a unit of kinetic order, an 18-fold concentration increase, for example, producing only a 3-fold rate increase. Then, the reactions, however rapidly they might start, were soon proceeding relatively slowly, much more slowly than could be ascribed to the consumption of reagents or the approach to equilibrium—for example, 5 times more slowly after only one-fifth of the realisable reaction. Furthermore, when tetramethylammonium chloride was initially introduced along with the corresponding fluoride, the reaction started much more slowly—for instance, by 21 times when the chloride ion was made equivalent to fluoride ion; and thereafter reaction continued with a much less pronounced progressive retardation.

These results were interpreted as illustrating unimolecular substitution, in the general case in which the ionisation step is significantly reversed, the overall-forward process containing two forward steps (1) and (3), of which step (1) is rate-controlling, together with one retrograde step (2), as follows:

$$\text{AlkCl} + \text{F}^- \underset{(2)}{\overset{(1)}{\rightleftarrows}} \text{Alk}^+ + \text{Cl}^- + \text{F}^- \overset{(3)}{\longrightarrow} \text{AlkF} + \text{Cl}^- \quad . \quad . \quad . \quad . \quad (S_N1)$$

The increase in initial rate with increasing concentration of the ionic reagent was attributed to a primary salt effect, which we could approximately calculate from our previous work on the unimolecular reactions of benzhydryl halides in aqueous solvents, by taking account of the difference of solvent with the aid of electrostatic theory. The progressive retardation of the continuing reaction, and the initial retardation produced by initially added tetramethylammonium chloride, as well as the weakened further retardation which then characterise the subsequent reaction, were consistently interpreted as effects of formed or added chloride ion in reversing the ionisation of the alkyl chloride.

The equation which gave a quantitatively satisfactory common description of the spontaneous retardations, and of the rate depressions induced by the addition of chloride ion, was the general kinetic equation of a unimolecular reaction,
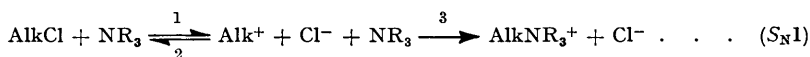
$$dx/dt = k_1(a - x)(c - x)/\{\alpha(b + x) + (c - x)\}$$

or, in its integrated form,

$$kt(a - c) = \alpha(b + c) \ln\{c/(c - x)\} + \{(a - c) - \alpha(a + b)\} \ln\{a/(a - x)\}$$

where *a*, *b*, and *c*, are the initial concentrations of the alkyl halide, the displaced halide ion, and the substituting agent, respectively, and *x* is the concentration converted at time *t*. Two constants are involved, k_1 the rate-constant of step 1, which broadly determines the absolute rates, and the retardation constant α, the ratio of the rate-constant of step 2 to that of step 3, which governs the retardations, spontaneous and induced.

Before a parallel study could be undertaken of a reaction of *m*-chlorobenzhydryl chloride with an amine in sulphur dioxide, an ancillary investigation had to be made, which has already been reported (Bateman, Hughes, and Ingold, *J.*, 1944, 243), into the condition of the amine molecule in sulphur dioxide solution. For it was known that amines form complexes with the solvent, and a theory had been promulgated to the effect that two amine molecules are combined in each such complex : this, if true, would have altered fundamentally an interpretation of kinetic results. However, it was shown by analysis, combined with ebullioscopic determinations of molecular weight, and measurements of electrical conductance, that the complexes have the composition NR_3SO_2, and that they are monomeric and essentially undissociated. Thus we know that one molecule of amine is present in each kinetically separate particle containing amine, and that, even though there is a specific solvation, the kinetically significant concentration of solvated amine is identical with the stoicheiometric molecular concentration of the amine The complexes do undergo slight homolytic dissociation into their components, as could be told from the appreciable partial vapour pressures of the latter, when together present in stoicheiometric ratio, excess of solvent having been removed. In addition, the complexes undergo some electrolytic dissociation in the sulphur dioxide solvent, to give ions, the precise nature of which is still unsettled. However, this also is a minor dissociation : the two amines used in the kinetic investigation now to be described, when at the concentrations employed, show conductances of the order of only 1% of those of typical strong electrolytes at similar concentrations.

In continuation of the earlier work on substitution in *m*-chlorobenzhydryl chloride by fluoride ion in sulphur dioxide, a study has been made of the kinetics of the reactions of the same alkyl chloride with pyridine and with triethylamine in that solvent, the temperature ($-10.75°$) being the same as before in order that rate constants for the reactions of the three substituting agents would be directly comparable. It had first to be determined whether the substitutions by the two amines, like the reaction of fluoride ion, are of unimolecular type :

$$AlkCl + NR_3 \underset{2}{\overset{1}{\rightleftharpoons}} Alk^+ + Cl^- + NR_3 \overset{3}{\longrightarrow} AlkNR_3^+ + Cl^- \quad . \quad . \quad . \quad (S_N1)$$

step 1 being rate-controlling; or whether the reactions of these strongly nucleophilic substituting agents are one-stage bimolecular processes :

$$AlkCl + NR_3 \longrightarrow AlkNR_3^+ + Cl^- \quad . \quad . \quad . \quad . \quad (S_N2)$$
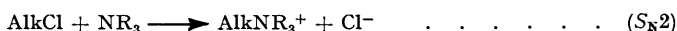
As before, the substitutions were kinetically followed by the changes in the electrical conductance of the solutions, as interpreted with the aid of empirically constructed calibration curves connecting the conductances with the concentrations of the products of substitution, in the presence of various concentrations of the materials introduced initially.

We shall explain in detail below that the reactions of pyridine and of triethylamine showed kinetic characteristics qualitatively similar to those of the reaction of fluoride ion, but with certain quantitatively distinctive effects, which we believe to signify mechanistic modifications of a more finely graded nature than would correspond to a simple switch from the unimolecular to the bimolecular mechanism of substitution.

The initial specific rates, $k_0 = (dx/dt)_{t=0}/a$, of any of these reactions, in the absence of initially added chloride ion ($b = 0$), should, if the substitutions are simply unimolecular, be equal to the rate constant k_1 of step 1 in that mechanism, that is, of the alkyl halide ionisation common to all the substitutions. Therefore, apart from salt effects, the initial rates k_0 of the different substitutions should be equal to one another and independent of reagent concentrations. If, however, some of the substitutions are bimolecular, then their initial specific rates k_0 should be equal to the second-order rate constant, different for each such substitution, of this one-stage mechanism, multiplied into the initial concentration of the substituting agent, in symbols, k_2c. And thus the initial specific rates, k_0, although different for the different substitutions following this mechanism, should for each of them converge on zero as the reagent concentration is diminished. If unimolecular

and bimolecular reactions run concurrently, then the rates k_0 should converge on a common finite value, as the concentration c is diminished.

Some initial specific rates of the reactions of *m*-chlorobenzhydryl chloride with pyridine and with triethylamine are given in Table 1. In Fig. 1, these values are compared with those previously recorded for the reaction with fluoride ion. It will be seen that the rates of the reaction with pyridine are about 3—5 times larger than those of the reaction with fluoride ion. The rates of the reaction with triethylamine are still larger, about 5—7 times larger than for the reaction with fluoride ion. These differences of rate, although small having regard to the general chemical differences between the reagents, are clearly real, and must be of significance for mechanism. Yet we see that, within the range of the observations, the initial specific rates of the different reactions tend neither to zero nor to any common finite value, as the reagent concentrations are diminished.
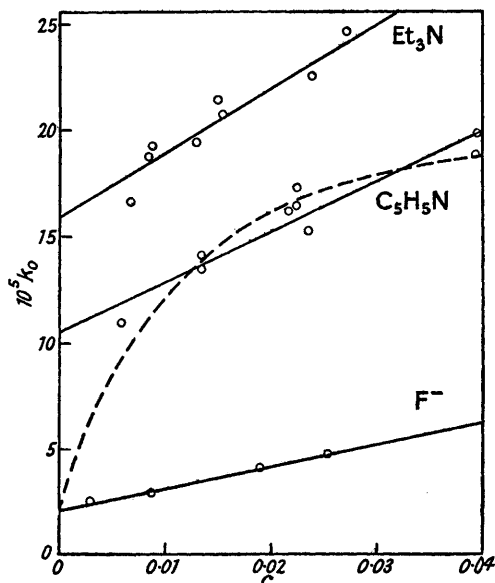

FIG. 1. *Nucleophilic substitution in* m-*chlorobenz-hydryl chloride by fluoride ion, pyridine, and triethylamine, in sulphur dioxide at* $-10.75°$: *initial specific rates* (k_0 *in sec.$^{-1}$) of reaction of the alkyl chloride as functions of the concentrations* (c *in mole/l.) of the substituting agents.*

For explanation of the broken (exponential) curve see p. 640.

As shown in Fig. 1, the initial specific rates of the reactions with the amines increase with the initial concentrations of the amines, for instance, by about 2-fold for a 7-fold increase in the concentration of pyridine, and by 1·5-fold for a 4-fold increase in that of triethyl-

TABLE 1. *Initial specific rates* (k_0 *in sec.$^{-1}$) of reactions of* m-*chlorobenzhydryl chloride with pyridine and with triethylamine in sulphur dioxide at* $-10.75°$.

	Pyridine				Triethylamine		
No.	[RCl]	[Amine]	$10^5 k_0$	No.	[RCl]	[Amine]	$10^5 k_0$
22	0·0427	0·0058	10·9	33	0·0520	0·0067	16·5
19	0·0428	0·0058	10·9	27	0·0460	0·0084	18·7
17	0·0432	0·0135	14·1	26	0·0465	0·0088	19·1
14	0·0433	0·0135	13·4	28	0·0447	0·0130	19·3
12	0·0433	0·0218	16·1	34	0·0520	0·0150	21·4
16	0·0446	0·0225	16·4	31	0·0540	0·0157	20·7
13	0·0446	0·0225	17·2	24	0·0420	0·0240	22·5
15	0·0471	0·0237	15·2	25	0·0473	0·0274	24·8
18	0·0396	0·0395	19·8				
21	0·0396	0·0396	18·8				

amine, the rate increase in either case being much smaller than would correspond to a unit of kinetic order in the substituting agent. But, because both pyridine and triethyl-amine are only weak electrolytes in sulphur dioxide, the rate increases are very much greater

than could be attributed to salt effects. Evidently these rate increases must be assigned to some other cause.

Even when a reaction with pyridine starts quickly, it is soon going forward quite slowly. This spontaneous progressive retardation is considerably stronger than that observed in the reaction with fluoride ions. A reaction with pyridine may typically be found, after not much more than one-tenth of its realisable course, to be continuing 10 times more slowly than it started. The kinetic effect of chloride ion, initially added as tetraethylammonium chloride, is similarly enhanced in the pyridine reaction. Thus the initial rate is reduced by about 60 times when the added chloride is equivalent to the pyridine. The continuing reaction then shows a much reduced progressive retardation, but still one which is stronger than for the fluoride-ion reaction. In the reaction of triethylamine, both the spontaneous progressive retardation, and the retardations induced by initial additions of chloride ion, are considerably smaller than in the reaction of pyridine. Thus a reaction with triethylamine may typically be going with one-quarter of its initial speed after one-fifth of its course. The initial reaction rate is reduced by about 17 times when tetraethylammonium chloride is initially introduced in quantity equivalent to the triethylamine. These retardations are, indeed, slightly milder than those applying to the fluoride-ion reaction.

As in the reaction with fluoride ions, so in these amine reactions, the spontaneous and induced retardations are obviously inexplicable on any scheme of bimolecular substitutions. By making use of the general kinetic equations for unimolecular substitution (p. 635), we previously accounted very exactly for the retardations found in the reaction of fluoride ion. As we shall show, the same procedure, when applied to the reactions of pyridine and triethylamine, leads to results which describe the general situation well, though with not quite the former quantitative precision.

Just as we obtained the main unimolecular rate constants k_1 from the initial rates of reactions in which no extraneous chloride ion had been introduced, so we may find the retardation constant α from the initial rates of reactions started in the presence of added chloride ion. It is easily verified from the equations given that, if ρ is the ratio b/c of the initial concentration of chloride ion to that of the amine, and if f is the factor $k_0^{(b)}/k_0$ by which the added chloride ion reduces the specific rate, then α is given by $(f^{-1} - 1)/\rho$. Some determinations of α, made by this method, for the pyridine and triethylamine reactions are recorded in Table 2.

TABLE 2. *Initial specific rates* ($k_0^{(b)}$ *in sec.*$^{-1}$) *of reactions of* m-chlorobenzhydryl chloride *with pyridine and with triethylamine in the presence of tetraethylammonium chloride in solvent sulphur dioxide at* −10·75°.

No.	[RCl]	[Amine]	[Salt]	ρ	$10^5 k_0^{(b)}$	f	α	Mean
			Pyridine					
41	0·0385	0·00523	0·00138	0·264	0·656	0·0560	64	
42	0·0482	0·00657	0·00178	0·271	0·608	0·0506	69	
43	0·0444	0·0223	0·00047	0·0211	7·40	0·467	54	60
44	0·0570	0·0272	0·00066	0·0243	7·01	0·413	58	
46	0·0463	0·0234	0·00086	0·0367	5·18	0·324	57	
			Triethylamine					
36	0·0526	0·0056	0·00234	0·418	2·47	0·140	14·7	
37	0·0507	0·0056	0·00111	0·198	3·55	0·202	19·8	16
39	0·0510	0·0150	0·00040	0·0267	14·7	0·720	14·7	
40	0·0426	0·0125	0·00041	0·0328	13·7	0·695	13·4	

In these determinations of the constants k_1 and α, we have in principle made no use, and in practice only a slight use, of the kinetic forms of the reactions; and thus it is allowable to employ the constants in order to calculate kinetic forms. It is also permissible to compare the results of such calculations with experimentally observed kinetic forms from the beginnings of reaction up to points earlier than those at which the overall retrograde reaction, which we have not yet studied separately, could disturb the measured rate. In the reactions of the two amines with *m*-chlorobenzhydryl chloride, the equilibria lie

well over on the side of the *m*-chlorobenzhydryl-pyridinium and -triethylammonium ions; *
and consistently, our study of the kinetics indicates that at least the first 10—20% of
these reactions, as conducted, can be treated as free from disturbances by the retrograde
substitutions.

For the reactions of pyridine and triethylamine, it was found that, whilst the equation
of the unimolecular mechanism reproduces the observed course of reaction incomparably
better than does that of the bimolecular mechanism, both equations being fitted to the
same initial rate, the unimolecular equation does not quite repeat the perfection of its
performance on the fluoride-ion reaction. The general concordance, and detailed deviations,
are illustrated in Fig. 2. However, we think that these quantitative discrepancies do not
affect our main conclusion that the approximate agreement of the observations with the
unimolecular equation demonstates the essentially unimolecular nature of the amine
substitutions. The disturbances might be connected with the finer modifications of
mechanism that we shall discuss below, but they might represent neglected effects of non-
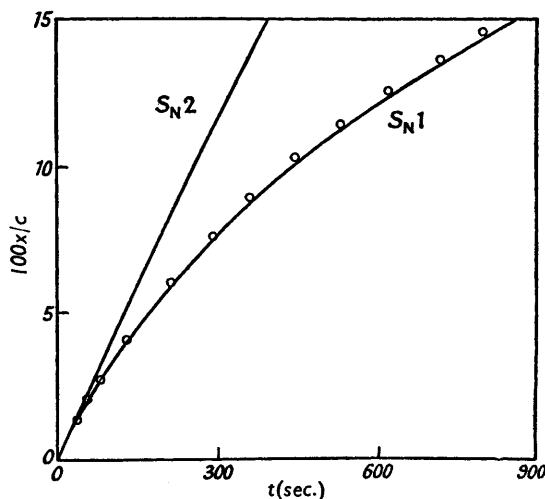ideality, or some experimental systematic error.

FIG. 2. *Kinetic course of reaction of* m-*chloro-
benzhydryl chloride with triethylamine in
sulphur dioxide at* —10·75° (*part of run*
35).

The summary of our findings is that the substitutions by amines show the most
diagnostic kinetic feature of the unimolecular mechanism, the common-ion retardations,
but deviate from the requirements of that mechanism in at least two important respects.
First, the rates are sensitive to the nature of the substituting agent, though not nearly as
sensitive as would be expected of bimolecular reactions. Secondly, the rates are affected
by the concentrations of the reagents, though not nearly to the extent appropriate to
bimolecular reactions.

It seems clear that, in moving over, with strongly nucleophilic substituting agents,
from hydroxylic solvents to a polar aprotic solvent, we have not changed a unimolecular
into a bimolecular substitution, but that we have introduced into the unimolecular reactions
some variation of mechanism suggestive of a partial incursion of bimolecular character.
If, however, we try to specialise this conclusion by assuming that, whilst most of the
individual molecular acts of substitution pursue the unimolecular mechanism, some of them
concurrently follow the bimolecular mechanism, an obvious difficulty arises. For then it

* We did not make any actual determinations of the position of equilibrium, but we did follow a
number of the runs to more than 70% of their stoicheiometrically possible course, when they were still
going forward slowly. The difficulty in determining equilibrium compositions by the technique used
for the kinetic measurements arose from the circumstance that, for convenience in filling, our con-
ductivity cells were only stoppered, and not hermetically sealed, with the result that a slow escape of
the sulphur dioxide solvent began, after some time, appreciably to alter concentrations, thereby limiting
significant conductance measurements to periods of about one day. These reactions, even though they
may start rapidly, go so slowly in the later part of their course that many days would have been needed
in order to establish a close approximation to equilibrium.

cannot be understood why rates which are sensitive to the nature of the substituting agent when the concentration of the latter is high, are, as Fig. 1 shows, hardly less sensitive when the concentration is low. This hypothesis of concurrent S_N1 and S_N2 processes would require Fig. 1 to exhibit three straight lines diverging from a common point on the rate axis.

We prefer to assume that, as was foreseen long ago (Hughes, Ingold, and Patel, *J.*, 1933, 526; Gleave, Hughes, and Ingold, *J.*, 1935, 236), the beginnings of a change from a unimolecular to a bimolecular mechanism are such that the individual molecular acts of substitution take on individual characters intermediate to various degrees between the two extremes of mechanism. We can then understand, though as yet only in a qualitative way, the general pattern of Fig. 1, in particular the seeming paradox that the sensitivity of rate to the nature of the reagent is itself insensitive to the reagent concentration.

Consider the following crude but simple model. We will assume that, in bimolecular substitution, an alkyl halide molecule has a negligible probability of decomposition, unless a reagent particle is localised to within a very small volume beside it, and that then it has a large probability of reaction. We assume also that, in unimolecular substitution, the alkyl halide molecule has a large probability of decomposition, independently of where any reagent particle may be. We can give these two situations a common description by assuming that, around any alkyl halide molecule, a certain volume v, which would be small in the bimolecular case but large in the unimolecular, can be described, such that, when no reagent particle is inside it, the probability of decomposition of the alkyl halide molecule is small at best, whereas when at least one reagent particle is within, the probability of reaction is large and characteristic. By now allowing v to vary without restriction from one reaction to another, we can conceptually connect the two limiting molecular mechanisms with a continuous chain of intermediate mechanisms. Certainly, our assumption that the reaction probability of the alkyl halide undergoes the whole of its increase at one point in the approach of a reagent particle, is a highly artificial simplification, which we would like to give up, assuming instead probabilities which vary smoothly with reagent position, and thereby bringing a further element of continuity into our picture. But as we do not know what functional connexion to assume, this path cannot be pursued, and we are left to consider what conclusions the simpler model has to offer.

Let n reagent particles be contained in a solution of volume V, so that the concentration c of the reagent equals n/NV, where N is Avogadro's number. Then the probability that at least one reagent particle is in a particular localised volume v is evidently *

$$1 - (1 - v/V)^n = 1 - e^{cNv}$$

provided that $v \ll V$. If k and K are respectively those specific rates of reaction of the alkyl halide, which would obtain if all alkyl halide molecules at all times had the low and the high reaction probability associated respectively with the non-occupation and the occupation of v by the reagent, then the initial specific rate corresponding to the calculated degree of occupation will be

$$(dx/dt)/a = k + K(1 - e^{-\beta c})$$

where $\beta = Nv$ is a constant of the reaction.

When β is small, the second term becomes $K\beta c$, and represents a reaction of first order in the reagent, and thus of second order overall. When β is large, the term becomes K, and represents a reaction of zero order in the reagent, and first order overall. Between these extremes the specific rate should rise with increasing reagent concentration, at first steeply and then ever more gently in an exponential way. Actually, we can put two exponential curves, both rising from the fluoride-ion intercept in Fig. 1, through the pyridine and the triethylamine points, without exposing deviations markedly larger than those from the best straight lines. One such curve is inserted in Fig. 1, but its introduction does not imply that our model is considered good enough to be tested by a precise mathematical form, or that our experimental data are accurate enough for such a comparison. Our main point is that the data present a picture which seems qualitatively

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* The first expression followed by counting complex ions, and the second derives from the theorem that $(1 - y/r)^r$ tends to e^{-y} as r tends to infinity.

more consistent with the theory of intermediate molecular mechanisms than with that of concurrent extremes.

Winstein, Grunwald, and Jones have previously attacked the problem of distinguishing between intermediate mechanisms and concurrent extremes, and have concluded that the aqueous-alcoholysis of *iso*propyl bromide is not satisfactorily regarded as a simple concurrence of extremes (*J. Amer. Chem. Soc.*, 1951, **73**, 2700). Our own preconceptions strongly favour this conclusion, but we must add that, in our view, the authors ensured it by their procedure. Their method was to demonstrate a disagreement between the observed effect of changes of solvent on the rate of this solvolysis, and the mixture-law sum of the two computed effects, one patterned, with the aid of a linear free-energy relation, on that of bimolecular solvolysis, as of methyl or (somewhat less safely) ethyl bromide, the relevant solvent property being nucleophilic power, and the other modelled similarly on that of unimolecular solvolysis, as of *tert.*-butyl bromide, the important solvent property here being ionising power. But in re-mapping the ethyl bromide pattern of kinetic solvent effects in order to obtain the bimolecular part of those of *iso*propyl bromide, a form of free-energy relation was adopted which involved cross-correlation with the unimolecular case of *tert.*-butyl bromide (and, in fact, the adopted relation, which had to be used as if linear, was manifestly non-linear for methyl and ethyl bromide). Thus the computed component effects, whose independence and complementality were to be tested, got mixed together before the test of additivity was applied.

Our retardation constants α give the following order for the rates of attack of reagents on the *m*-chlorobenzhydryl carbonium ion, $Cl^- > NEt_3 > F^- > C_5H_5N$, the rate-ratios being as the reciprocals of the numbers 1, 16, 20, 60. From this it would seem that, for attack upon a pre-formed cation, the long-range forces of the net charge are an important determinant of the affinity of the reagent, as well as the short-range forces of its unshared electrons, and, conceivably, of steric effects.

EXPERIMENTAL

The preparation and purification of materials, together with the apparatus and the method of measurement, were those described by Bateman, Hughes, and Ingold (*loc. cit.*). Pyridine was purified through its zinc chloride complex. In the kinetic runs with the two amines, the amine was added to the solvent in the conductivity cell, and the electrical conductance was allowed to settle down, before the *m*-chlorobenzhydryl chloride was added and a series of readings started. Initial disturbances were minimised by care in the exclusion of moisture, as controlled by the initial freedom of the solution from the yellow colour which immediately develops when moisture does intrude.

Calibration.—Owing to the difficulty in handling dry samples of *m*-chlorobenzhydryl-pyridinium and -triethylammonium chloride, which are extremely hygroscopic, the effect of different concentrations of them on the electrical conductance was determined by causing them to be formed in various amounts in sulphur dioxide solution from suitable quantities of the reactants. After time had been allowed for the production of a salt, but always at a moment when the reaction was not going too quickly, the increment of conductance was noted, and the cell-contents were immediately cooled to $-80°$. The cooled solution was extracted with ether and water, and the aqueous chloride ion was determined by electrometric titration with silver nitrate. In this way, concentration–conductance curves were built up, first for *m*-chlorobenz-hydryl-pyridinium and -triethylammonium chloride in the absence of any added salt, and then for each of them in the presence of various amounts of initially added tetraethylammonium chloride. The curves were not quite linear, and gave factors, connecting concentration increments with conductance increments, which ranged from 0·040 mole ohm cm.$^{-2}$ for *m*-chloro-benzhydrylpyridinium chloride, and 0·066 mole ohm cm.$^{-2}$ for *m*-chlorobenzhydryltriethyl-ammonium chloride, both at low concentrations, to about double these values at the highest total salt concentrations used.

Results.—The initial specific rates are given in Tables 1 and 2. For most runs without initially added tetraethylammonium chloride, direct reading of the conductance–time graphs was found to be unreliable, owing to the large rate changes near the commencement of reaction. It was more satisfactory to read from these graphs a series of rates over the first few units per cent. of reaction, and then to plot the reciprocals of these rates against the extent of reaction, the initial rate being obtained from the axial intercept of the new graph. Independent repeti-

tions by this method gave reasonable consistency, and mean values were taken. For most runs in which tetraethylammonium chloride had been added initially, the direct and the indirect method were about equally satisfactory and we usually made several independent estimates by both methods and took a selected mean.

TABLE 3. *Kinetic course of the reaction of* m-*chlorobenzyhydryl chloride with pyridine in sulphur dioxide at* $-10.75°$ *(run 13).*

Initially, $a = [\text{RCl}] = 0.0446\text{M}$, and $c = [\text{C}_5\text{H}_5\text{N}] = 0.0225\text{M}$. The product concentration is x (M) at time t (sec.). The bimolecular rate constant, k_2 in sec.$^{-1}$ mole^{-1} l., is calculated as $\{1/t(a-c)\}\ln\{c(a-x)/a(c-x)\}$. The unimolecular rate constant, k_1 in sec.$^{-1}$, is computed from the equation on p. 635 with $\alpha = 60$.

t	10^4x	$10^2x/c$	10^4k_2	10^5k_1	t	10^4x	$10^2x/c$
45	2·00	0·89	46	15·8	1,530	18·24	8·12
66	2·80	1·25	42	18·2	1,692	18·64	8·27
120	4·00	1·78	34	17·0	1,872	19·48	8·64
186	4·64	2·06	25	14·2	2,100	20·64	9·16
240	5·85	2·60	25	15·7	2,292	21·20	9·41
285	6·72	2·99	23	16·8	2,460	21·84	9·71
360	7·80	3·46	22	17·0	2,670	22·66	10·09
468	9·08	4·03	20	16·8	2,880	23·28	10·33
594	10·68	4·74	19	17·4	3,120	24·12	10·70
678	11·68	5·19	18	18·0	3,300	24·76	10·99
732	12·24	5·45	17	18·1	3,480	25·40	11·29
900	13·56	6·02	16	17·8	3,630	25·92	11·50
1080	14·84	6·80	14	17·6	3,780	26·40	11·72
1218	15·84	7·05	14	17·7	4,020	27·20	12·51
1290	16·28	7·23	13	17·5	70,200	77·76	34·50

Part of the course of a run with triethylamine is shown in Fig. 2. In further illustration of the kinetic form of these reactions, Table 3 records the followed part of a pyridine run. The calculated rate constants in the Table apply to a period well before the effects of overall reversibility begin to be apparent in the measurements.

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