236. *Mechanism of Substitution at a Saturated Carbon Atom. Part LIV.* Kinetics of Chlorine Exchange between Triphenylmethyl Chloride and Tetra-*n-*butylammonium Chloride in Benzene.*

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The kinetics are studied of the exchange of chlorine between triphenyl-methyl chloride and tetra-*n*-butylammonium radiochloride in benzene at 25—45°. In these conditions the reaction is of first order in triphenyl-methyl chloride, and of zeroth order in the salt at all concentrations up to saturation.

This kinetic form and rate are practically unaffected by added tetra-*n*-butylammonium perchlorate, which undergoes no stoicheiometric reaction with triphenylmethyl chloride. But the kinetic form is changed, and the initial rate is reduced by added tetra-*n*-butylammonium azide, which concurrently produces the relatively inert substance, triphenylmethyl azide, though not rapidly enough to preclude observation of the strong initial retardation produced by the salt. This retardation is identified as the kinetic " mass-law effect " in an S_N1-type reaction, as described in 1940 for unimolecular solvolysis and for other unimolecular substitutions.

The rate of exchange is much increased by added nitromethane or nitro-benzene, without disturbance to the first-order form of the runs. The initial rate of exchange is considerably increased by added pyridine, or tri-*n*-butyl-amine, though now such a disturbance arises, apparently, from reversible interaction between the triphenylmethyl chloride and the amine. The initial rate of exchange is greatly increased by added methyl alcohol, benzyl alcohol, or phenol, which, as reaction continues, produce some kinetic disturbance arising from the concurrent, relatively slow, formation of an ether. All these catalytic effects, whether by non-reacting polar solutes, such as the nitro-compounds, or by reacting ones, such as the hydroxy-compounds, have the common characteristic that, notwithstanding a contrary report by Swain and Kreevoy, they display no integral kinetic order which remains uniform over a significant concentration range. The number and position of these catalyst molecules in the transition state of the rate-controlling step of the measured process are thus capable of correct description only in the statistical terms appropriate to macroscopic co-solvent effects, and there is no necessary and unique placing of a single molecule of catalyst, as is required by Swain's " push-pull " theory.

It was verified that in the presence of added methyl alcohol the zeroth order of exchange with respect to tetra-*n*-butylammonium chloride is preserved. Added tetra-*n*-butylammonium perchlorate now appears to have a mildly retarding effect on the exchange.

Some part of the significance of these results is indicated, and further comment on them is made in the comparative discussion in Part LVIII.

Our object being to discover what happens to a nucleophilic substitution with a very strong tendency to use the unimolecular mechanism, S_N1, when it is transferred to an ionophobic solvent, *i.e.*, a solvent which can barely support free ions, we should probably in any case have elected to study the kinetics of the nucleophilic substitutions of triphenyl-methyl chloride in benzene. But, in fact, this choice of a system for investigation was settled for us by the circumstance that the general field was not a clear one. For eight years, publications have been appearing on this particular group of reactions, and a series of statements has been made about their kinetic orders, from which conclusions have been drawn as to their mechanism, and, by extension, as to the mechanism of nucleophilic substitutions in general. And as these more general conclusions have been held to over-throw the picture of nucleophilic substitution previously set up by two of us, we

felt we ought to form an opinion as to how far the kinetic descriptions given were accurate, and to what extent they supported the body of conclusions which had been built on them.

Following our paper on the electrolytic condition of salts in benzene, we now present four papers recording severally our version of the kinetics of four nucleophilic substitutions of triphenylmethyl chloride in benzene, first, two substitutions by anionic reagents, and then, two by reagent molecules. Our exploration of the electrolytic situation assists interpretation of the kinetic evidence relating to the anion substitutions. This study in turn prepares the way for the problem of the kinetics of the molecular substitutions, our interpretation of which makes use of the preceding electrochemical plus kinetic experience. The four kinetic papers, of which this is the first, are mainly concerned with description and classification, *i.e.*, with kinetics, and only to a small extent with conclusions concerning mechanism, since some repetition is avoided by dealing, as we do, with the common features of interpretation in a separate paper (Part LVIII), where we attempt to synthesise from them a partial picture of ionic reactions in benzene.

We start here with the simplest of the nucleophilic substitutions, the " symmetrical " substitution of halogen exchange between triphenylmethyl chloride and isotopically labelled chloride ion, supplied in the form of a quaternary ammonium chloride. This reaction has been investigated previously by Swain and Kreevoy,[1] who employed as their salt dimethyldi-*n*-octadecylammonium chloride, which they were not able to get even analytically pure, and therefore, as we would think, not nearly pure enough for reliable reaction kinetics. Another obvious comment on this salt is that, having the structure of a cationic soap, its properties as an electrolyte, which they did not determine, might not be completely normal. However, with this material, the rate of halogen exchange was found to be independent of its lowest concentrations, but then at a certain point to start rising with the 3·7th power of the concentration.

Preferring to use an isotropic and smaller cation, we supplied chloride ion as tetra-*n*-butylammonium chloride, the anion of which contained ^{36}Cl, so that the reaction of exchange could be followed radiochemically.

(1) *Kinetic Form of the Exchange Reaction.*—The kinetics of the exchange in benzene were studied at 25—45°. The uptake of radioactive chlorine by the triphenylmethyl chloride was of first order in triphenylmethyl chloride, and first-order constants, $k_1 = d[R*Cl]/[RCl]dt$, did not depend on the concentration of that substance. These first-order rates were also independent of the concentration of tetra-*n*-butylammonium chloride

TABLE 1. *Rate-constants (k_1 in sec.$^{-1}$) of exchange of chlorine between triphenylmethyl chloride (RCl) and tetra-n-butylammonium radiochloride (M$^+$Cl$^-$) in benzene.*

Run	[RCl]	[M$^+$Cl$^-$]	$10^5 k_1$	Mean	Run	[RCl]	[M$^+$Cl$^-$]	$10^5 k_1$	Mean
		At 25·0°					*At 30°*		
M 81	0·01	0·00078	0·258		P 41	0·02	0·00250	0·533	
M 84	,,	0·00114	0·350		P 10	0·05	0·00150	0·503	
M 82	,,	0·00206	0·333		P 6	,,	0·00250	0·490	
M 83	,,	0·00378	0·300		P 8	,,	,,	0·475	
M 98	,,	0·00390	0·342		P 13	,,	,,	0·500	
M 80	,,	0·00393	0·308		P 34	,,	,,	0·547	
M 72	0·05	0·00250	0·352	0·320	P 35	,,	,,	0·483	
		At 44·6°			P 5	,,	0·00500	0·500	
M 102	0·05	0·00250	1·68		P 7	,,	,,	0·495	0·503
M 103	,,	,,	1·67						
M 104	,,	,.	1·70	1·68					

over an experimental range, limited on the low side by the requirements of accuracy, and on the high side by the solubility of the salt. Thus the reaction is of zeroth order in salt. We shall attach significance in Part LVIII, not only to the form of the result, but also to the absolute values of the rates, and both are illustrated in Table 1.

[1] Swain and Kreevoy, *J. Amer. Chem. Soc.*, 1955, **77**, 1122.

The mean rate constants fit the Arrhenius equation $k_1 = B \exp(-E/\mathbf{R}T)$ with $B = 1.7 \times 10^6$ sec.$^{-1}$, and $E = 16.0$ kcal./mole. The low B value points to a transition state with a precisely defined, and probably somewhat elaborate, geometry, which, along with the consequent constitution of E, is discussed in Part LVIII.

(2) *Kinetic Effects of Added Salts.*—We have examined the effect on exchange rate of three classes of added substances, *viz.*, salts, dipolar aprotic molecules, and hydroxylic compounds. First, as to salts, we have used two, tetra-*n*-butylammonium perchlorate, which does not engage in any stoicheiometric reaction with triphenylmethyl chloride, and tetra-*n*-butylammonium azide, which reacts to produce the relatively inert substance, triphenylmethyl azide. In our conditions, the saline perchlorate has no appreciable influence, either on the kinetic form of the exchange reaction or on its rate. On the other hand, the saline azide both reduces the exchange rate, and introduces a side-reaction. The side-reaction arises because the azide converts some of the triphenylmethyl chloride into unreactive triphenylmethyl azide, and non-radioactive chloride ion. However, the interesting point is that the *initial* rates of exchange are reduced by the added azide. The results in Table 2 will illustrate these points.

TABLE 2. *Effects of added salts* (M^+X^-) *on rate constants* ($k_1{}^a$ *in* sec.$^{-1}$) *of exchange of chlorine between triphenylmethyl chloride* (RCl) *and tetra-*n*-butylammonium radiochloride* (M^+Cl^-) *in benzene at* 30°.

Run	[RCl]	[M^+Cl^-]	[M^+X^-]	$10^5 k_1{}^a$ (obs.)	$10^5 k_1{}^a$ (calc.)
Without added salts (steady first-order rate) :					
Table 1	0.02—0.05	0.0015—0.0050	—	0.503	—
*Added tetra-*n*-butylammonium perchlorate (steady first-order rate)* :					
P 12	0.05	0.0025	0.00020	0.495	—
*Added tetra-*n*-butylammonium azide (initial rates cited)* :					
P 32	0.05	0.0025	0.0025	0.25	0.25
P 31	0.05	0.0025	0.0125	0.07	0.08
P 42	0.02	0.0025	0.0040	0.18	0.19
P 43	0.02	0.0040	0.0040	0.30	0.25

The result last mentioned shows that radiochloride ion and azide ion are not separately attacking triphenylmethyl chloride molecules, or anything else that is freely available at the rate at which they can attack it. Obviously, the two anions are competing for something in limited supply. This competition is of the same nature as what was called the kinetic " mass-law effect " in the unimolecular mechanism of substitution, S_N1, as described in 1940 for the solvolysis of benzhydryl (diphenylmethyl) halides in aqueous acetone,[2] and for non-solvolytic substitutions of these halides in solvent sulphur dioxide,[3] and as predicted then for substitutions of triphenylmethyl halides.[4] Swain, Scott, and Lohmann subsequently observed it in the latter field, but describe their observations as if unaware of the precedents.[5] Essentially, the effect consists in the retardation of a reaction, rate-controlled by the production of an active form, when the reagent, which, left to itself, would consume the whole of this in completing the reaction being measured, finds a competitor, added or arising, with which it must contend. The simplest way in which one could demonstrate this type of effect in a radiochemically followed chloride-ion exchange, is to add a chemically different, irreversibly acting, anion, and note whether the initial rate of exchange is affected.

There must be some ratio of the specific rates of attack of chloride ion and of azide ion on the active intermediate. An assumption that this ratio is unity gives a fair account of the rate reductions, as can be seen from the last column of Table 2, where the figures are

[2] Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979.
[3] Bateman, Hughes, and Ingold, *J.*, 1940, 1017.
[4] *Idem, ibid.*, p. 960.
[5] Swain, Scott, and Lohmann, *J. Amer. Chem. Soc.*, 1953, **75**, 136; cf. also ref. 1.

computed on that basis. Bearing in mind the considerable experimental error in initial rates, it is suggested only that the ratio may be taken as unity to within $\pm 20\%$.

The above means, for example, that if we add azide ion in quantity equivalent to the chloride ion, the rate of chloride exchange is cut by about one-half, and that if we add five times as much, it is cut to about one-sixth. It would be easy at this point to jump to the conclusion that the loss of rate is equal to the rate of the concurrent formation of triphenylmethyl azide; but that is not so. It will be shown in the next paper (Part LV, Section 1) that this azide is in fact formed much more rapidly, though its formation rate is in turn cut by an added saline chloride according to a law of just the same form. Moreover, the concurrent chloride exchange, thereby permitted, has a rate much smaller than would be equivalent to the loss in the rate of formation of triphenylmethyl azide. The meaning of these apparent paradoxes is considered in Part LVIII (Section 2).

(3) *Kinetic Effect of Added Non-hydroxylic Polar Molecules.*—As rate-influencing molecular substances of the polar but non-hydroxylic class, we investigated two nitrocompounds and two tertiary amines. Nitromethane and nitrobenzene accelerate the chlorine exchange, without disturbing the first-order form of the runs. However, no simple relation is revealed by the results in Table 3, between the rate increase and the

TABLE 3. *Effect of added polar aprotic solutes* (PA) *on rate constants* ($k_1{}^{pa}$ *in* sec.$^{-1}$) *of exchange of chlorine between triphenylmethyl chloride* (RCl) *and tetra-n-butylammonium chloride* (M^+Cl^-) *in benzene.*

Run	Temp.	[RCl]	[M^+Cl^-]	[PA]	$10^5 k_1{}^{pa}$
No added substances (steady first-order rates) :					
Table 1	25°	0·01—0·05	0·0008—0·0025	—	0·320
,,	30	0·02—0·05	0·0015—0·0050	—	0·503
Added nitromethane (steady first-order rates) :					
M 65	25°	0·10	0·0026	1·09	15·8
M 66	,,	,,	0·0025	2·18	64·5
M 67	,,	,,	,,	3·27	~470
P 29	30	0·05	,,	0·37	2·67
Added nitrobenzene (steady first-order rates) :					
M 15	25°	0·01	0·0025	0·05	0·63
M 55	,,	,,	,,	0·20	1·34
M 54	,,	,,	,,	0·39	1·67
M 52	,,	0·04	,,	0·97	2·30
M 59	,,	0·09	,,	1·95	5·67
M 60	,,	0·01	,,	3·90	35·2
M 63	,,	,,	0·0050	,,	31·7
M 61	,,	,,	,,	4·87	89
M 62	,,	0·09	,,	6·82	~520
P 30	30	0·05	0·0025	0·97	2·90
Added pyridine (falling specific rates : initial value cited) :					
M 22	25°	0·10	0·0025	0·10	0·88
Added tri-n-butylamine (falling specific rates : initial value cited) :					
M 38	25°	0·10	0·0025	0·10	1·36

concentration of nitro-compound producing it. For example, if we plot the logarithm of the excess rate in the presence of nitrobenzene against the logarithm of the nitrobenzene concentration, we obtain a smoothly curving plot with no suggestion of linearity at any integral gradient : the reaction has no " kinetic order " with respect to nitrobenzene. We conclude that we are dealing with a transition state, which the polar solute stabilises in a statistical way, without accepting any close or precise placing in the transition state. In other words, we are observing a macroscopic co-solvent effect by a dipolar substance on a polar reaction.

Added pyridine and tri-*n*-butylamine increase the initial rate of chlorine exchange, but cause the specific rate of the continuing reaction to fall progressively. Interesting changes

are observed when the triphenylmethyl chloride and tertiary base are pre-mixed, before the radioactive salt is added and the measurements are commenced.   In the case of pyridine, the initial rate is reduced, but the specific rate of the continuing reaction falls much less steeply.   In the case of tri-*n*-butylamine, the initial rate is further increased by this procedure.   There is undoubtedly a reaction, probably a reversible one, between the triphenylmethyl chloride and the tertiary amines, to give materials, presumably quaternary ammonium salts, with different potentialities from that of the original triphenylmethyl chloride, for conversion into triphenylmethyl radiochloride.   The forward rates of the reactions with the amines must be comparable to the rate of chlorine exchange of triphenylmethyl chloride.   If we assume that triphenylmethyl radiochloride is formed less easily from the pyridine product, but more easily from the tri-*n*-butylamine product, than from original triphenylmethyl chloride, and also that the tertiary bases exert a dipolar co-solvent catalysis, analogous to that of the above nitro-compounds, then the whole rather complicated set of results can be understood.   In the reaction with pyridine, for example, the catalysis causes the reaction to start more rapidly even though some material is being concurrently side-tracked.   This side-tracking produces a progressive radioactive-dilution of chloride ion, and that is why the *apparent* specific rate of the continuing reaction falls.   If we pre-mix the triphenylmethyl chloride and the base, this last disturbance will already have had much of its effect before measurements are commenced.   We do not describe these experiments in detail, because the reaction they are elucidating is to be the subject of a future paper.   Just two runs are cited in Table 3 to show that, in spite of the side-tracking of triphenylmethyl chloride by reaction with the tertiary bases, the initial rate of chlorine exchange is increased in their presence.   In these runs, opportunity for preliminary interaction was reduced to a minimum by adding the triphenylmethyl chloride last.

(4) *Kinetic Effect of Added Alcohols and Phenol.*—We have examined the kinetic effect on halogen exchange of three added hydroxy-compounds, methyl alcohol, benzyl alcohol, and phenol.   All these substances react with triphenylmethyl chloride to produce, reversibly, triphenylmethyl ethers and hydrogen chloride.   In their forward direction, these reactions are slower than the chlorine exchange.   Thus in the presence of 0·1M-methyl alcohol, the methyl-alcoholysis (*i.e.*, ether formation) has a rate of only one-eighth of that of the chlorine exchange.   Benzyl-alcoholysis and phenolysis are slower still.

TABLE 4.   *Effect of added hydroxy-compounds* (R'OH) *on the initial specific rates* (k_1^{al} *in* sec.$^{-1}$) *of exchange of chlorine between triphenylmethyl chloride* (RCl) *and tetra*-n-*butyl-ammonium chloride* (M^+Cl^-) *in benzene.*

Run	Temp.	[RCl]	[M⁺Cl⁻]	[R'OH]	$10^5 k_1^{al}$	Run	Temp.	[RCl]	[M⁺Cl⁻]	[R'OH]	$10^5 k_1^{al}$
No added substance :						*Added benzyl alcohol* :					
Table 1	25°	0·050	0·0025	—	0·32	P 36	30°	0·050	0·0025	0·002	0·88
,,	30	,,	,,	—	0·50	P 37	,,	,,	,,	0·004	1·17
						P 38	,,	,,	,,	0·008	2·0
Added methyl alcohol :						P 39	,,	,,	,,	0·016	4·2
M 97	25°	0·100	0·0041	0·002	0·48	P 40	,,	,,	,,	0·024	8·2
M 96	,,	0·098	,,	0·005	0·55	P 14	,,	,,	,,	0·050	37
M 90	,,	0·097	0·0010	0·020	2·58						
M 89	,,	0·095	0·0024	,,	1·93	*Added phenol* :					
M 88	,,	0·096	0·0041	,,	1·97	P 26	30°	0·050	0·0025	0·001	1·2
M 91	,,	0·097	0·0082	,,	1·90	P 27	,,	,,	,,	0·002	2·55
M 94	,,	0·100	0·0022	0·040	6·8	P 28	,,	,,	,,	0·003	6·7
M 92	,,	,,	0·0043	,,	7·7	P 25	,,	,,	,,	0·005	22
M 93	,,	0·098	0·0075	,,	6·1						
M 95	,,	0·101	0·0136	,,	6·0						
M 99	,,	0·099	0·0044	0·100	44·7						

Hence the disturbance that these ether-forming reactions would progressively introduce into the kinetics of the exchange process, by their consumption of triphenylmethyl chloride, can be entirely avoided by measuring initial exchange rates.   A series of initial

specific rates of exchange, showing the kinetic effects of the three hydroxy-compounds, are given in Table 4.

The results for the three hydroxy-compounds have the common characteristic that they indicate no particular " order " with respect to hydroxy-compound. If we plot the logarithm of the rate increase produced by added methyl alcohol, against the logarithm of the concentration of methyl alcohol, we obtain a steepening curve, with a gradient rising from zero, or a little above, to slightly more than 2, but with no visible arrest of gradient at unity, or at any other value. The rates for benzyl alcohol give a somewhat similar curve, the gradient of which rises steadily from less than 1 to more than 2, as illustrated in the Figure. The phenol curve is generally steeper, but is otherwise similar, the gradient now rising from less than 2 to about 3, without indication of an arrest.

We conclude that, like the polar aprotic solutes, these hydroxylic solutes are furnished neither in uniform small numbers, nor in precisely defined locations, to the transition

Specific rates of chlorine exchange between triphenyl-methyl chloride and tetra-n-butylammonium chloride in benzene at 30° : plot of the logarithm of the rate catalysed by benzyl alcohol against the logarithm of the concentration of benzyl alcohol.

The straight lines indicate theoretical slopes for kinetic orders of 1 and 2 with respect to benzyl alcohol. Catalysis by methyl alcohol and by phenol is described similarly by smoothly bending curves.
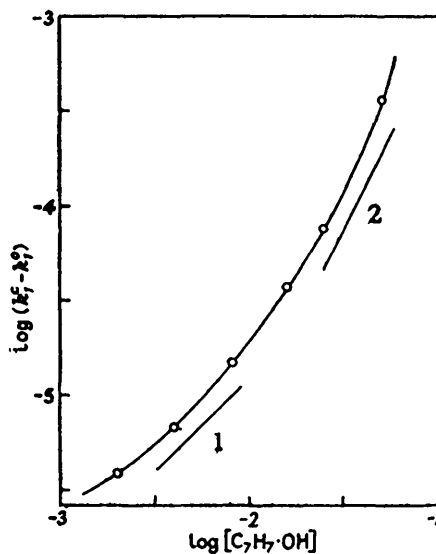
state of the reaction stage which is rate-controlling for the measured process. The numbers and positions of these kinetically accessory molecules are in principle capable only of statistical description. The forces by which they stabilise the polar transition state must be electrostatic, and must be exerted from varying distances, as is not difficult to understand when one realises how far electrostatic forces can extend in the benzene solvent (preceding paper). This is just the type of kinetic effect which we classify as a macroscopic co-solvent effect.

The only one of these catalytic effects on which Swain and Kreevoy report is that of phenol; and their description of it differs from ours. Their claim is that the increase of rate obeys a simple second-order law,

$$\text{Rate} = k_2[\text{RCl}][\text{PhOH}]$$

said to be valid for salt up to 0·007M, and phenol up to 0·011M; *i.e.*, the order is unity in phenol. No numerical data are offered in substantiation of this statement, which our results do not support. But the equation is set down, and it is emphasised verbally that the catalysed rate is proportional to the first power of phenol concentration over a consider-able range; and then these unsupported statements are used as a starting point for the development of a theory of mechanism. Anticipating some of the following papers, we may mention that this is only one of a number of allegedly simple and exact reaction-orders, which Swain has claimed to have established, and has made the foundation of his

mechanistic theories, but which are not confirmed in the present re-investigation.   In one of Swain's papers it is argued,[6] that catalytic effects of hydroxy-compounds definitely cannot be co-solvent effects, " because the benzene is in more than a hundred-fold excess over the hydroxy-compound."   It is added that they therefore " must be due to the termolecular mechanism " (which Swain regards as universal).   This is W. Taylor's argument over again [7] (except that Taylor wanted to make the bimolecular mechanism universal).   We thought that an unmistakable reply had been made to this,[8] but the general pattern of Taylor's papers is nevertheless reproduced in those of Swain.*

For the purpose of interpreting our investigations, described in accompanying papers, of the kinetics of the ether-forming reactions of triphenylmethyl chloride, we had to know whether the addition of the alcohols needed as reagents, would, or would not, seriously modify the zeroth-order character, with respect to salt, of the exchange of chlorine between triphenylmethyl chloride and an added saline chloride.   Because the measured process is one of isotopic exchange, the discussion we have offered so far does not cover this point. We have, however, checked it experimentally, and two small groups of experiments, relating to kinetic order with respect to salt in the presence of methyl alcohol, are included in Table 4.   They show that, for two different concentrations of methyl alcohol, the concentration of salt can be varied over a 6-fold or 8-fold range without introducing any systematic change into the initial specific rate of exchange.   The reaction of triphenyl-methyl chloride with methyl alcohol to give the mixed ether is considerably slower than the concurrent exchange of chlorine with an added saline chloride.   Thus it would seem that the exchange preserves its kinetic form, *i.e.*, both its first order in triphenylmethyl chloride, and its zeroth order in salt, in the presence of reactive added substances, including those which greatly alter the rate of exchange, provided that the rate of reaction with the added substance is only a small, or somewhat small, fraction of the rate of exchange.

(5) *Kinetic Effect of Adding both an Alcohol and Another Salt.*—Our reason for investigating this matter will be made fully clear in Part LVIII : for the present, we explain it in outline only.

It has been shown that the exchange of chlorine between triphenylmethyl chloride and tetra-*n*-butylammonium chloride in benzene is not noticeably catalysed by tetra-*n*-butyl-ammonium perchlorate (Section 2), but that it is catalysed by added alcohols (Section 4). It will be shown in Parts LVI and LVII that the reactions of triphenylmethyl chloride with alcohols are strongly catalysed by tetra-*n*-butylammonium perchlorate.   Evidence has already been presented to show that the exchange reaction with tetra-*n*-butyl-ammonium chloride depends on a rate-controlling step in which the saline substituting agent is not involved (Section 1).   Evidence will be given, in Part LVI particularly, to the effect that the reactions with alcohols involve a rate-controlling step in which the substituting agent does not necessarily participate.   Reviewing these conclusions, one naturally thinks first of the simple possibility that all the substitutions have their rates fully determined by a single common process.   But, if that were so, and if that process

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* A very recent case, not dealt with elsewhere in the present papers, of the tendency illustrated to assign reaction orders on totally inadequate evidence is contained in the paper by Swain, Kaiser, and Knee [9] on the nuclear alkylation of pyrrole by reaction of a triarylmethyl chloride with pyrrole in benzene.   A transient colour is produced, the intensity of which was measured as a function of time and reactant concentration. The calculated curve for the rise and fall of colour fits the observational points, but in principle the calculation requires three disposable rate constants to be chosen, and in fact a fourth disposable constant, in the form of the equilibrium constant of an additional assumed equi-librium, was introduced in order to produce the fit obtained—which was then obtained despite a 4-fold discrepancy of intensity in an attempted identification of the colour source, and despite the fact that the samples of impure original chloride were coloured, with intensities up to about 70% of the maximum transient intensity measured.   This unsatisfactory situation is not entirely clearly described, but is deducible from figures given.

[6] Swain, *J. Amer. Chem. Soc.*, 1948, **70**, 2989.
[7] Taylor, *J.*, 1937, 1853; 1939, 478; *J. Amer. Chem. Soc.*, 1938, **60**, 2094.
[8] Bateman, Church, and Hughes, *J.*, 1940, 913; Church and Hughes, *ibid.*, p. 920.
[9] Swain, Kaiser, and Knee, *J. Amer. Chem. Soc.*, 1955, **77**, 4681.

can be catalysed by tetra-*n*-butylammonium perchlorate, *i.e.*, by-passed by an alternative reaction-path involving the perchlorate, in the substitutions with the alcohols, then it should also be so catalysed and by-passed in the substitution with tetra-*n*-butylammonium chloride, provided that the conditions are made the same. We make the conditions the same if we study the effect of tetra-*n*-butylammonium perchlorate on the chlorine exchange reaction in the presence of, say, methyl alcohol. We have already prepared the ground for such experiments by showing (Section 4) that, in the presence of methyl alcohol, just as in its absence, the rate of chlorine exchange is independent of the concentration of tetra-*n*-butylammonium chloride. It remains, then, to determine whether this first-order reaction, when methyl alcohol is present, is catalysed by added tetra-*n*-butylammonium perchlorate. As Table 5 shows in two examples, the exchange is not catalysed by perchlorate in these conditions.

TABLE 5. *Effect of tetra-n-butylammonium perchlorate* ($M^+ClO_4^-$) *on the first-order rate constants* ($k_1{}^{p-\alpha}$ *in sec.$^{-1}$) of exchange of chlorine between triphenylmethyl chloride* (0·1M *throughout*) *and tetra-n-butylammonium chloride* (M^+Cl^-) *in the presence of methyl alcohol in benzene at* 25°.

Run	$[M^+Cl^-]$	[MeOH]	$[M^+ClO_4^-]$	$10^6 k^{p-\alpha}$
M 96	0·0041	0·005	—	0·55
M 100	0·0041	,,	0·000135	{~0·53 initial, falling. 0·39 mean to 30% reaction.
M 92—M 95	0·0022—0·0136	0·040	—	6·6
M 101	0·0040	,,	0·00197	{~5·9 initial, falling. 5·0 mean to 40% reaction.

Actually, the exchange runs, in the presence of methyl alcohol and the perchlorate, start at about the rate at which they would go had the perchlorate been omitted, or perhaps somewhat more slowly, and then show a continuing retardation. Because the latter effect is superimposed on the counting fluctuations inseparable from radiochemical measurements, we cannot be quite sure that the recorded small diminution of initial rate, chiefly noticeable at the higher perchlorate concentration, is real; but it probably is, and could be understood if it were (cf. Part LVIII, Section 3). The continuing retardation is definitely real, and probably has a cause similar to that of the progressive retardation shown by the exchange reaction in the presence of pyridine (Section 3); in the present case, a concurrent methyl-alcoholysis produces chloride ion, which effects a progresive radioactive dilution of the tetra-*n*-butylammonium radiochloride, so that the rate of uptake of radioactivity by the triphenylmethyl chloride becomes diminished by a cause not taken into account in the computation of the rate constant, which accordingly falls as reaction proceeds. It is consistent that it thus falls less in the presence of more methyl alcohol, because direct measurement shows that the more methyl alcohol (above 0·002M) one adds, the less methyl-alcoholysis occurs relatively to exchange (Part LVI, Section 3), at first sight a surprising relation, which, however, can also be understood (Part LVIII, Section 3).

For the moment, the important result is that exchange is not catalysed by perchlorate, in conditions in which alcoholysis is catalysed. This shows that there is not just one rate-determining stage, which is common to both substitutions, despite the demonstrations given, and to be given, with respect to the kinetic orders of these reactions. Here we will not go beyond this negative conclusion: the positive conclusion to which the result contributes must wait until we can set other results beside it, as is done in Part LVIII.

EXPERIMENTAL

Materials.—It is convenient to describe in one place, and we choose this one, the preparation or purification of all the substances used in the work of this set of six papers, whether or not they were required for the work of the present paper.

First, as to triphenylmethyl chloride, no method of purification could be found by which

the commercial material could be used as starting point for the preparation of kinetically satisfactory samples, even though it could be very easily purified sufficiently to have the correct m. p. and give good analytical data. We therefore prepared our own triphenylmethyl chloride from methyl benzoate and phenylmagnesium bromide by way of triphenylmethanol.[10] The product was crystallised first from light petroleum–benzene containing acetyl chloride, and then repeatedly from light petroleum–benzene. The crystals were dried at 60° over phosphoric oxide in an oil-pump vacuum.

Benzene of " AnalaR " quality was refluxed for 12 hr. with, and distilled fractionally from, molten potassium. Calcium hydride was tried as a drying agent :[11] the product was as good, but not better. The main impurity in a solution of triphenylmethyl chloride, say, 0·05 or 0·1M, in benzene, as prepared for kinetics, was acid, presumably hydrogen chloride arising from adventitious moisture. With the arrangements at our disposal, we could reduce this unwanted acid to 10^{-5}M, but not lower; and some experiments were done with solutions in which it had reached higher values, 10^{-4}M or more. We therefore treated it as part of the routine in these kinetic studies to examine the effect of deliberately added hydrogen chloride on the reactions being examined, in order to assess their sensitiveness to any disturbance which might be caused by adventitious hydrogen chloride. In the experiments described in this paper, hydrogen chloride in traces is not a dangerous impurity, because it is largely inactivated as a catalyst by tetra-*n*-butylammonium chloride, which was present in all the experiments. (This effect is due to the formation of the hydrogen dichloride ion.)

The tetra-*n*-butylammonium salts were prepared from tri-*n*-butylamine (freed by the Hinsberg procedure from primary and secondary amines) and *n*-butyl iodide, both carefully fractionated before use. The quaternary iodide, crystallised from ethyl acetate–light petroleum, had m. p. 145° (Found : I, 34·35. Calc. for $C_{16}H_{36}NI$: I, 34·4%). It was converted into the nitrate with the aid of silver nitrate[13] (Found : C, 63·9; H, 12·0. Calc. for $C_{16}H_{36}O_3N_2$: C, 63·1; H, 11·8%), and into the perchlorate with silver perchlorate[13] (Found : C, 56·2; H, 10·9; N, 4·0; Cl, 10·0. Calc. for $C_{16}H_{36}O_4NCl$: C, 56·2; H, 10·6; N, 4·1; Cl, 10·4%). The last salt was another material which we found easy so to purify that it gave good analytical figures, and an m. p. close to its maximum, but difficult so to purify that it gave an unalterable minimum rate to reactions highly sensitive to catalysis. The material we found acceptable by this criterion had the characteristic that, after repeated crystallisation from ethyl acetate–light petroleum and drying for some days in an oil-pump vacuum over phosphoric oxide, the m. p. was about 199°; but that after some weeks of further drying, the m. p. rose to, and remained steady at, 203—204°. *Tetra-*n-*butylammonium azide* was made by basifying the iodide with a suspension of silver oxide in ethyl alcohol, and neutralising the solution with ethereal hydrazoic acid : after removal of the solvent under reduced pressure, the salt was obtained as a hygroscopic solid, which was precipitated repeatedly from benzene solution with light petroleum, crystallised from benzene, and given a period of prolonged drying in an oil-pump vacuum over phosphoric oxide (Found : C, 68·0; H, 13·1. $C_{16}H_{36}N_4$ requires C, 67·7; H, 12·7%). The *chloride* was similarly produced, except that the neutralisation was with aqueous hydrochloric acid, and, in so far as the radioactive chloride was required, with hydrochloric acid containing [36]Cl. The salt was repeatedly crystallised from light petroleum–benzene, and then was melted and kept at 100° with continued pumping in order to remove solvent of crystallisation (Found : C, 69·4; H, 13·1; Cl, 12·7. $C_{16}H_{36}NCl$ requires C, 69·2; H, 13·0; Cl, 12·8%). All these tetra-*n*-butylammonium salts crystallise from benzene in a very voluminous form containing benzene of crystallisation, which can be removed by pumping. A few experiments were made with tetraethylammonium chloride, which was crystallised from ethyl alcohol containing ether (Found : Cl, 21·4. Calc. for $C_8H_{20}NCl$: Cl, 21·4%).

Purchased nitromethane was refluxed under nitrogen with activated charcoal, and was dried, first with calcium chloride, and then with phosphoric oxide, with filtration after each stage. It was then distilled (b. p. 100·5—101·0°), passed through a column of freshly dried chromatographic alumina, then again distilled and passed through alumina. Methyl alcohol was dried in the magnesium–iodine reaction. Nitrobenzene, benzyl alcohol, and phenol, were purified conventionally. Benzyl triphenylmethyl ether, prepared from triphenylmethyl

[10] *Org. Synth.*, 1943, **23**, 98, 100.
[11] Brown, Levin, and Abrahamson, *J. Chem. Phys.*, 1951, **19**, 1226.
[12] Cox, Kraus, and Fuoss, *Trans. Faraday Soc.*, 1935, **31**, 751.
[13] Luder, Kraus, Kraus, and Fuoss, *J. Amer. Chem. Soc.*, 1936, **58**, 255.

chloride, benzyl alcohol, and triethylamine,[14] and crystallised from ethyl ether–light petroleum, had m. p. 101—102°.

Kinetic Methods.—All glass apparatus was given a prolonged baking at 150° before work with benzene solutions. The tetra-*n*-butylammonium radiochloride was weighed directly into a graduated flask, most of the benzene to be used was added, and the salt was dissolved, its dissolution being hastened by warming if necessary. Any further materials, other than triphenylmethyl chloride, to be included in the run were then added, and the solution was brought to the experimental temperature. Finally, the triphenylmethyl chloride was introduced in previously prepared benzene solution. Samples of 5 ml. were withdrawn, then and subsequently, and were run into 10 ml. of ligroin (b. p. 100—120°), which precipitated the salt completely; and after 1 min. or longer the solution was filtered through a No. 4 sintered-glass Pyrex filter. Runs in the presence of hydroxy-compounds, *e.g.*, methyl alcohol, produce some hydrogen chloride, but this is probably held back with the salt as tetra-*n*-butylammonium hydrogen-dichloride, leaving triphenylmethyl chloride as the only radioactive compound in the filtrate. The radioactivity of the filtrate was measured in a liquid-counting tube of conventional type, and then the triphenylmethyl chloride in the filtrate was determined; for some is adsorbed on the precipitated salt, and, in some experiments, a part is destroyed by a side-reaction. This measurement was made either by electrometric titration with silver nitrate after dilution with moist acetone, or by acidimetric titration with sodium hydroxide or tri-*n*-butylamine after complete hydrolysis with moist acetone, these methods giving identical results. The total radioactivity of the reaction mixture was determined by running one sample into 10 ml. of benzene, instead of ligroin, and going through the same analytical routine (except for the now unnecessary filtration).

Small modifications of this general procedure had to be introduced in certain cases. In fast runs, the ligroin was pre-cooled, in order to minimise radioactive exchange with the precipitated salt during filtration. In some runs involving nitrobenzene, more than 10 ml. of ligroin had to be used to render the precipitation of salt complete. In runs involving tri-*n*-butylamine, the triphenylmethyl chloride could be estimated by silver titration only after acidification with perchloric acid.

Rate constants, whether for a complete run or in the measurement of initial rates, were deduced from the formula :

$$k_1 = \frac{2 \cdot 303 b}{(a+b)t} \log \left\{ 1 - \frac{x_0}{C}\left(1 + \frac{b}{a}\right)\right\} \Big/ \left\{ 1 - \frac{x}{C}\left(1 + \frac{b}{a}\right)\right\}$$

where *t* is the time, *a* and *b* are the concentrations of triphenylmethyl chloride and tetra-*n*-butylammonium radiochloride, respectively, x_0 and *x* are the counting rates, corrected for background, at the kinetic time-zero and at time *t*, respectively, and *C* is the total counting rate of the reaction mixture, corrected for background and then further corrected for the loss of triphenylmethyl chloride in the filtered samples. A convenient way to use this formula is to plot log $\{1 - (a + b)x/aC\}$ against *t*, and multiply the slope of the line by $-2 \cdot 303b/(a + b)$.

TABLE 5. *Examples of chlorine-exchange runs.*

Run P 7		Run M 55		Run M 38		Run M 95	
[RCl] = 0·05M		[RCl] = 0·10M		[RCl] = 0·10M		[RCl] = 0·10M	
[Buⁿ₄NCl] = 0·0050M		[Buⁿ₄NCl] = 0·0025M		[Buⁿ₄NCl] = 0·0025M		[Buⁿ₄NCl] = 0·0136M	
In benzene at 30°		[Ph·NO₂] = 0·20M		[Buⁿ₃N] = 0·10M		[MeOH] = 0·040M	
C = 1760 min.⁻¹		In benzene at 25°		In benzene at 25°		In benzene at 25°	
		C = 80·1 min.⁻¹		C = 73·4 min.⁻¹		C = 362·0 min.⁻¹	
t (min.)	*x* (min.⁻¹)	*t* (min.)	*x* (min.⁻¹)	*t* (min.)	*x* (min.⁻¹)	*t* (min.)	*x* (min.⁻¹)
1	20	0	5·1	0	16·0	0	10·5
23	131	5	11·0	2	19·8	1	19·0
65	308	10	28·2	5	24·2	2	24·8
89	420	20	34·3	10	29·5	5	59·2
120	521	40	56·9	20	38·1	10	83·8
185	768			30	45·6	15	123·7
252	989			60	59·2	20	150·0
390	1278						

Results.—A representative selection of rate-constants is given in Tables 1—4. The type of experimental basis on which these figures rest is illustrated in Table 5. In runs M 38 and

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[14] Norris and Young, *J. Amer. Chem. Soc.*, 1930, **52**, 753.

M 95, the first three points essentially determine an initial rate, since the reaction-order does not remain first throughout, owing to the progressive removal of triphenylmethyl chloride, and the progressive radioactive dilution of chloride ion, by the side-reaction involving the added substance.

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