237. *Mechanism of Substitution at a Saturated Carbon Atom. Part LV.*[*] *Kinetics of the Reaction of Triphenylmethyl Chloride with Tetra-*n*-butylammonium Azide in Benzene.*

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Contrary to Swain and Kreevoy, the reaction between triphenylmethyl chloride and a quaternary ammonium azide in benzene is not a simple second-order process, that is, one of first order in each reagent. It is approximately of first order in triphenylmethyl chloride; but, at concentrations of tetra-*n*-butylammonium azide sufficiently low to avoid a large formation of multipolar ions, the reaction is approximately of zeroth order in the salt. It is true that the first-order rate constant with respect to triphenylmethyl chloride falls as reaction continues; but that is not due to the progressive disappearance of azide ion, implying a non-zero order in azide, but to the progressive appearance of chloride ion, which exerts the mass-law retarding effect so characteristic of the S_N1 mechanism. Indeed, the reaction follows the general kinetic equation of this mechanism. Consistently, initially added tetra-*n*-butylammonium chloride reduces the initial rate, at concentrations at which added tetra-*n*-butylammonium perchlorate has no effect, and added extra tetra-*n*-butylammonium azide has scarcely any effect on the rate. The initial rate reductions are in approximately quantitative accord with the kinetic form of the continuing reaction.

Swain and Kreevoy claim that the reaction between triphenylmethyl chloride and a quaternary ammonium azide, when catalysed by phenol in benzene, is a third-order process, an example of Swain's "push-pull" mechanism, though it is stipulated that, in computing the kinetics, allowance must be made for an assumed complex between the azide and the phenol, a complex which puts the azide out of action but not the phenol. Our results reveal no definite kinetic order with respect to phenol, and no indication of the supposed complex. We conclude that there is no unique placing of just one phenol molecule in the transition state of the phenol-catalysed substitution.

These kinetic findings are discussed further in Part LVIII.

Having examined the symmetrically reversible substitution of triphenylmethyl chloride by chloride ion in benzene, we thought that the next simplest case to take up would be that of a practically irreversible substitution by some anion such as azide ion. Supplied as a quaternary ammonium azide, this anion reacts quantitatively with triphenylmethyl chloride in benzene, to produce triphenylmethyl azide, which suffers no further change in any of the conditions used in the present experiments.

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[*] Part LIV, preceding paper.

A kinetic description of this substitution has previously been given by Swain and Kreevoy,[1] who supplied azide ion in a sample of dimethyldi-*n*-octadecylammonium azide which was not analytically pure,* low as that standard of purity might be regarded in its application to a material intended for kinetics. Even had the salt been pure, its constitution, as a cationic soap, might have introduced uncontrolled electrolytic abnormalities. The authors describe the reaction as one of second order, *i.e.*, first order in triphenylmethyl chloride, and first order in the saline azide. They conclude that the substitution is of bimolecular type, and that a two-step mechanism, based on prior ionisation, with azide intervention in the second step, is excluded.

We supplied azide ions as tetra-*n*-butylammonium azide. We know that the electrolytic properties of this salt, in benzene at 30°, like those of the corresponding chloride, as well as those of mixtures of the two, are normal (Part LIII). This is important, because such mixtures must arise in the reaction we are to consider, *viz.*, the reaction between triphenylmethyl chloride and tetra-*n*-butylammonium azide in benzene at 30°.

Our main difficulty has been to find the region of concentration clear of those theoretical and practical obstacles that guard it like Scylla and Charybdis. For purposes of theoretical interpretation, we want a maximum of electrolytic simplicity: we would like our tetra-*n*-butylammonium azide to exist nearly wholly as one species, the ion pair, though a small proportion of quadrupoles would not matter, nor, probably, would simple and triple ions, which, although they will certainly be more chemically active than any neutral species, will be present in the extremely minute proportions illustrated in Part LIII. All this means working at considerable dilutions: it is clear, indeed, that we ought not to go up to salt concentrations much higher than 10^{-3}M. For, as Fuoss and Kraus [2] showed, the conductances of sufficiently soluble quaternary ammonium salts in benzene, a class of salt to which our azide belongs, rise sharply from 10^{-2}M to 10^{-1}M-salt, owing to the formation, in this concentration region, of charged aggregates higher than quadrupoles. At 10^{-1}M-concentration and beyond, these charged aggregates arise in considerable proportion, and, as they are very likely to be more chemically active than uncharged ion pairs, their relatively abundant formation may well lead to anomalous reaction kinetics.

That is one limitation. The counter-obstacle is that, for the purpose of getting good rate figures, *i.e.*, figures which are experimentally precise, independently of whether or not they can be interpreted, we would have liked to use these higher concentrations. Our analytical method can be made to work fairly well at salt concentrations in the neighbourhood 10^{-1}M or 10^{-2}M, but it loses accuracy at 10^{-3}M and below. Our " middle-course " has therefore been to conduct the critical kinetic experiments at azide concentrations from one to several units times 10^{-3}M. It is true that we have followed some of the kinetic phenomena into higher salt concentrations, but that was rather to see what happens when we disregard theoretically prescribed restrictions, than to obtain data for the purpose of deriving definite mechanistic conclusions. In this last matter, one is saved as usual by the circumstance that the more interesting mechanistic conclusions normally arise from the grosser kinetic phenomena, to demonstrate which high precision is not essential. The reasons why we had no need to raise these important questions of principle in the preceding paper are that the solubility of the saline reagent with which that paper deals, tetra-*n*-butylammonium chloride, is low enough to be itself a safe-guard, and that the employed radiochemical method of analysis is well suited to work at low concentrations.

(1) *Kinetic Form of the Reaction and the Effects of Added Salts.*—Unlike the reaction of

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* It is recorded that one sample of the azide contained 18% of something which would not react with triphenylmethyl chloride.

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

[2] Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 3614; Luder, Kraus, Kraus, and Fuoss, *ibid.*, 1936, **38**, 255; Strong and Kraus, *ibid.*, 1950, **72**, 166.

triphenylmethyl chloride with tetra-*n*-butylammonium radiochloride, that with tetra-*n*-butylammonium azide, even at low concentrations, does not follow the simple first-order rate law. First-order constants, k_1, for the specific rate of disappearance of triphenylmethyl chloride, $-d[RCl]/[RCl]dt$, fall progressively (Table 3). As is our practice in such cases, we deferred trying to decide the cause of this, until we had pursued the investigation further by measurement of initial specific rates, k_1°. These can always be calculated from the observations, without making any, possibly prejudicial, assumptions as to kinetic form.

A set of initial specific rates is shown in Table 1. The Table includes an illustration of the result that these first-order constants in triphenylmethyl chloride do not depend significantly on the concentration of that substance. How the constants depend on the concentration of tetra-*n*-butylammonium azide is best appreciated with the help of Fig. 1, where the logarithms of rate are plotted against the logarithms of salt concentration. We see that, as long as this concentration is below 10^{-2}M, the rate depends but little on it, but that from 10^{-2}M to 10^{-1}M the rate rises somewhat sharply, as we expected from our knowledge of the electrolytic situation. Quite formally, we may say that the kinetic order of reaction with respect to salt is approximately zero below 10^{-2}M, and that it rises from just above zero to about two between 10^{-2}M and 10^{-1}M. We also notice that, in this rise, there is no obvious arrest at an order of unity, *i.e.*, the curve in Fig. 1 has no pronounced flat at unit slope.

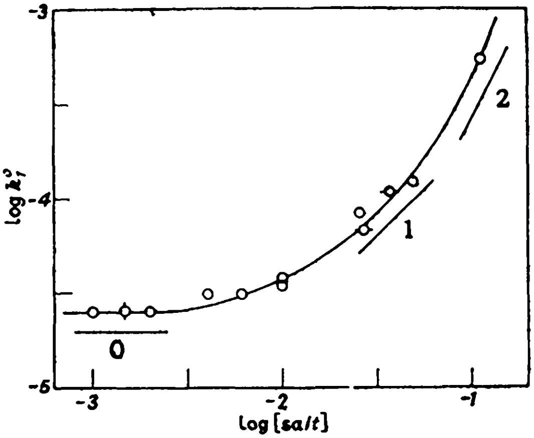

FIG. 1. *Reaction of triphenylmethyl chloride with tetra-*n*-butylammonium azide in benzene at 30°; plot of the logarithm of the initial specific rate of disappearance of triphenylmethyl chloride* versus *the logarithm of the total salt concentration:*

○ *Without any salt other than the azide.*

*With added tetra-*n*-butylammonium perchlorate.*

-○- *With added tetra-*n*-butylammonium nitrate.*

The short straight lines indicate theoretical slopes for kinetic orders of 0, 1, and 2 with respect to tetra-*n*-butylammonium azide

TABLE 1. *Initial specific rates* ($k_1^\circ = \{-d[RCl]/[RCl]dt\}_0$ *in sec.*$^{-1}$) *of reaction of triphenylmethyl chloride* (RCl) *with tetra-*n*-butylammonium azide* ($M^+N_3^-$) *in benzene at* 30°.

Run	$[RCl]_0$	$[M^+N_3^-]_0$	$10^5k_1^\circ$	Run	$[RCl]_0$	$[M^+N_3^-]_0$	$10^5k_1^\circ$
412	0·02	0·0010	2·5	406	0·05	0·0100	3·4
411	,,	0·0020	2·5	221	,,	0·0250	8·5
410	,,	0·0040	3·2	220, 222, 223	,,	0·0500	12
409	,,	0·0060	3·2	225	,,	0·1120	55
407	,,	0·0100	3·8				

We may now consider how Swain and Kreevoy supported their claim that their reaction has an order of unity with respect to azide. First, they stated that second-order rate constants could be calculated from the runs; but they did not give any figures to show the actual course of a run. Secondly, they gave just three calculated second-order rate constants, which are mutually inconsistent. If we multiply these constants by the initial salt concentrations in order to get initial specific rates, k_1°, and then plot these values against the salt concentrations, as in Fig. 2, then Swain and Kreevoy's summary of the kinetics amounts to joining these points by a straight line going through (or near) the origin. However, if it were permissible to derive any relation from only three points, it would seem more natural to join them by some curve, such as that illustrated. Moreover, regard being paid to the concentrations involved, such a curve would be generally consistent with our results, as summarised in Fig. 1. But without that comparison, and quite empirically, the three cited figures, if they indicate anything, indicate some curve, such as is shown in Fig. 2; and this curve, like our curve in Fig. 1, expresses, not an order of unity in salt, but an order rising continuously with concentration from well below unity to well above it.

FIG. 2.

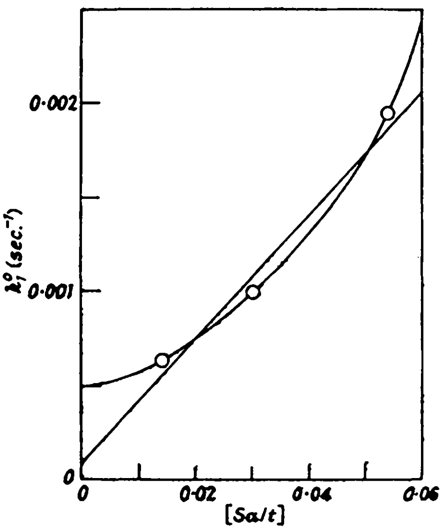

FIG. 3.

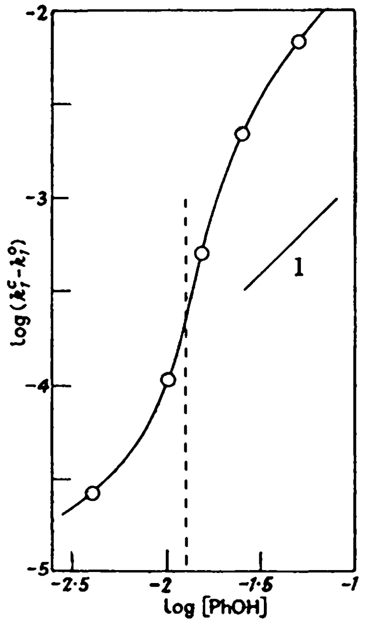

FIG. 2. *Swain and Kreevoy's data for the reaction of triphenylmethyl chloride with dimethyldi-*n*-octadecylammonium azide in benzene at 60°; plot of initial specific rates versus salt concentration.* This is the total numerical evidence given for the conclusion that the reaction is of first order in the salt. The straight line expresses this conclusion, and the curved line an alternative type of conclusion discussed in the present text.

FIG. 3. *Effect of phenol on the initial specific rates of reaction of triphenylmethyl chloride with tetra-*n*-butylammonium azide in benzene at 30°: plot of the logarithm of the catalysed rate against the logarithm of the concentration of phenol, other concentrations being constant.* The short line has the theoretical slope for an order of unity with respect to phenol. If only the excess of azide over phenol were kinetically effective, rates to the left of the vertical broken line would be zero.

Our next step was to examine the effect of added salts, the measurement still being that of initial rates. Some results are in Table 2. The only non-reacting salt we had was tetra-*n*-butylammonium perchlorate. This has no detectable kinetic effect, in the range of its solubility, which is within the range of concentration over which tetra-*n*-butylammonium azide itself has no effect on the rate. As a more soluble salt, we had available tetra-*n*-butylammonium nitrate, which probably does react with triphenylmethyl chloride, but to produce triphenylmethyl nitrate, which will subsequently, and very quickly, be converted into triphenylmethyl azide. This salt also, in its comparatively high concentration, appeared to have no more marked effect on the rate than its equivalent of extra tetra-*n*-butylammonium azide would have had. These effects are illustrated in Fig. 1.

Significant results arose from the addition of tetra-*n*-butylammonium chloride, which depressed the initial rate at all total salt concentrations up to at least as far as 0·02M. A set of results, applying to the important dilute range, below 0·008M, is included in Table 2.

TABLE 2. *Effect of added salts* (M^+X^-) *on initial specific rates* ($k_1°$ *in sec.*$^{-1}$) *of consumption of triphenylmethyl chloride* (RCl) *by reaction with tetra*-n-*butylammonium azide* ($M^+N_3^-$) *in benzene at* 30°.

M^+X^-	Run	$[RCl]_0$	$[M^+N_3^-]_0$	$[M^+X^-]$	$10^5k_1°$	
					(Obs.)	(Calc.)
$Bu^n_4NClO_4$	412	0·02	0·0010	—	2·5	—
	417	,,	,,	0·0005	2·6	—
$Bu^n_4NNO_3$	Interpltd.	0·05	0·0125	—	3·8	—
	238	,,	,,	0·0145	6·7	—
	239	,,	,,	0·0236	11·0	—
Bu^n_4NCl	Interpltd.	0·02	0·0025	—	2·6	—
	416	,,	,,	0·0025	1·5	1·3
	410	,,	0·0040	—	3·2	—
	415	,,	,,	0·0025	2·3	2·0
	414	,,	,,	0·0040	1·4	1·6

These rate depressions show that the reaction of tetra-*n*-butylammonium azide on triphenylmethyl chloride cannot be of first order in salt, and cannot have a bimolecular mechanism. Clearly, this salt and tetra-*n*-butylammonium chloride are in sharp competition for something the supply of which is limited : the two salts are certainly not attacking any freely available substance, such as molecular triphenylmethyl chloride : if they were, neither could have a depressing effect on the initial rate of reaction of the other. We are evidently observing here the so-called " mass-law effect," first demonstrated in 1940 for the solvolytic [3] and non-solvolytic [4] substitutions of benzhydryl (diphenylmethyl) halides, and predicted at that time [5] for analogous substitutions of triphenylmethyl halides. Swain, Scott, and Lohmann subsequently observed such effects by the method of the antecedent work.[6] However, Swain has based much mechanistic speculation in part on his inability to observe the mass-law effect in reactions of triphenylmethyl chloride with hydroxylic reagents in benzene,[7] but, as will be seen also from accompanying papers, this effect has proclaimed its presence to us in every one of Swain's reactions that we have re-investigated.

There must be some ratio (called α) in which tetra-*n*-butylammonium chloride and azide concurrently attack the slowly formed intermediate. As illustrated in the last column of Table 2, the rate depressions are fairly well represented if we assume that that ratio is unity, though the errors in the determination of the initial rates are such that we should not regard this value as fixed to better than ±20%. This means, for example, that the saline chloride, added in quantity equivalent to the azide, cuts the rate of azide substitution to one-half. However, this loss of rate does not represent the rate at which the saline chloride ion itself enters into reaction : we know the latter rate from work with radiochloride ion (Part LIV, Section 1), and it is much smaller. Yet this chloride-exchange rate is itself reduced by added saline azide according to a law of just the same form. The significance of these peculiar relations is discussed in Part LVIII (Section 2).

We can now consider the kinetic form of the reaction between triphenylmethyl chloride and tetra-*n*-butylammonium azide. The fact that the specific rate, calculated as a first-order constant in triphenylmethyl chloride, falls as reaction progresses, is obviously not to be explained by assuming that the reaction is of first order, or any other non-zero order, in the salt : the reaction does not proceed continually more slowly because this azide is

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[3] Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979.
[4] Bateman, Hughes, and Ingold, *J.*, 1940, 1017.
[5] Bateman, Hughes, and Ingold, *J.*, 1940, 960.
[6] Swain, Scott, and Lohmann, *J. Amer. Chem. Soc.*, 1953, **75**, 136; cf. also ref. 1.
[7] Swain, *J. Amer. Chem. Soc.*, 1948, **70**, 1119; 1950, **72**, 2790.

disappearing; for, when we take most of it away at the outset, the reaction does not (in the dilute range) go more slowly. The reason why the reaction slows down as it progresses is that tetra-*n*-butylammonium chloride is appearing. We are, indeed, observing once more the mass-law effect of an S_N1 reaction, and in just the form in which it was originally noticed in the S_N1 reactions of benzhydryl halides.

We can account for the progressive fall of specific rate, to within the accuracy of the measurements, on the basis of the kinetic outline,

$$\mathrm{RCl} \underset{k_2(\mathrm{Cl}^-)}{\overset{k_1}{\rightleftharpoons}} \mathrm{R}^+ \xrightarrow[(\mathrm{N}_3^-)]{k_3} \mathrm{RN}_3$$

with $k_1 \ll k_2, k_3$, and $k_2/k_3 = \alpha$. The normal object of our kinetic experiments is to derive initial specific rates, k_1°, because we can do that without making any hypothesis as to mechanism. These rates are the limiting initial values (as $x \longrightarrow 0$) of first-order rate constants $k_1^{(x)}$, calculated from familiar standard formulæ, which are identical with those which would apply to the above reaction scheme in the special case $\alpha = 0$, *viz.*:

$$\mathrm{d}x/\mathrm{d}t = k_1^{(x)}(a - x) \qquad k_1^{(x)}t = \ln \{a/(a - x)\}$$

where a is the initial concentration of triphenylmethyl chloride. The mass-law being into account, *i.e.*, on the assumption that $\alpha \neq 0$, these equations become generalised to:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1 \frac{(a - x)(b - x)}{b - x + \alpha x} \qquad k_1 t = \left(1 - \frac{\alpha a}{a - b}\right) \ln \frac{a}{a - b} + \left(\frac{\alpha b}{a - b}\right) \ln \frac{b}{b - x}$$

where b is the initial concentration of tetra-*n*-butylammonium azide. The constant α is disposable, but is not very critical: any values from about 0·8 to 1·2 will usually give fair agreement with our data.

In illustrating the application of these equations, we have to explain that, in order to get the best possible initial specific rates from our not always very accurate analytical determinations, we habitually reduced the latter in two ways, of which the first was mainly treated as a check, whilst the second was regarded as leading to the more reliable initial rates k_1°. In method (1), $k_1^{(x)}$ was calculated directly from the observations, by using the integrated first-order equation, and the set of values so obtained was plotted to give k_1° by extrapolation. In method (2), which was preferred, a smooth curve, giving the best (visual) fit to the observations, was drawn, and $k_1^{(x)}$ was similarly calculated for a series of points along it; and then these values were plotted, so affording k_1° by extrapolation. In Table 3 we show this type of treatment for a sample run, but with the addition that, in association with each method, the constant k_1 also is calculated by means of the generalised form of the integrated equation, with α set equal to 1·2. The constants are nearly as good if we take α as 1·0.

In the preceding paper, it was shown that the chloride-exchange substitution of triphenylmethyl chloride in benzene has the most diagnostic characteristics of an S_N1 type of mechanism. We have just shown that the corresponding azide substitution also has those characteristics. These independent conclusions are based on the internal evidence derived from the study of each reaction separately. The simplest trial synthesis of the conclusions would be that obtained by supposing that both substitutions have their rate determined by one and the same slow process. However, the absolute rates show that the real situation cannot be so simple. The specific rate of chloride exchange at 30° is $0{\cdot}50 \times 10^{-5}$ sec.$^{-1}$. In similarly dilute solution, the specific rate of azide substitution at 30° is $2{\cdot}5 \times 10^{-5}$ sec.$^{-1}$. In each case, then, we have a substitution of triphenylmethyl chloride, which is insensitive to the concentration of the substituting agent, but is sensitive to its nature. Here we only point out this interesting fact: we shall discuss it in Part LVIII.

(2) *Catalysis by Phenol.*—Swain and Kreevoy [1] examined the catalytic effect of phenol on the reaction between triphenylmethyl chloride and dimethyldi-*n*-octadecylammonium azide. They describe the kinetics as third-order, after account is taken of the alleged formation of a remarkable type of complex between the azide and the phenol, a complex which puts its contained azide completely out of action, but makes no difference to its contained phenol, so that the kinetic equation becomes

TABLE 3. *Kinetic form of the reaction between triphenylmethyl chloride and tetra*-n-*butylammonium azide in benzene at* 30°. *Constants for a unimolecular mechanism without* ($k_1^{(x)}$) *and with* (k_1) *allowance for mass-law retardation produced by the formed chloride ion.*

[Run 406. Initially $a = [Ph_3CCl]_0 = 0{\cdot}05$, and $b = [Bu^n_4NN_3]_0 = 0{\cdot}01$M. Percentage reaction, x, is $100x/x_\infty$ with $x_\infty = 0{\cdot}01$M. Time, t, is in min. and all k's are in sec.$^{-1}$.]

Method (1)				Method (2)			
x (%)	t	$10^5k_1^{(x)}$	10^5k_1	x (%)	t	$10^5k_1^{(x)}$	10^5k_1
7·2	7	3·28	3·62	2·5	2·5	3·33	3·37
				5	5	3·33	3·42
10·8	11	3·27	3·53	10	11	3·05	3·25
				15	17	2·98	3·28
14·8	18	2·82	3·05	20	24	2·83	3·27
				25	31	2·75	3·28
22·5	27	3·00	3·33	30	38	2·72	3·32
				35	47	2·58	3·30
34·0	42	2·60	3·55	40	57	2·58	3·28
				45	69	2·28	3·22
59·0	126	1·68	2·80	50	81	2·18	3·20
$10^5k_1°$ (by extrapn.)		3·4	—	(By extrapn.)		3·4 *	—
10^5k_1 (mean)		—	3·31	(Mean)		—	3·29

* This is the figure entered in Table 1. All other figures in Tables 1, 2, and 4 are similarly derived.

$$\text{Rate} \propto [\text{RCl}]([\text{Azide}] - [\text{Phenol}])[\text{Phenol}]$$

the middle factor being allowed its true value only if it is positive, and being taken as zero if in fact it is negative. Their summary of their kinetic findings is presented without any numerical support whatever: one figure is given, which is said to be a mean of third-order rate constants calculated thus for three runs, to which no individual reference is made. This is the sole basis on which it is concluded that the reaction is of termolecular type (called "third-order" in this paper), and, furthermore, that a two-step mechanism, based on ionisation, and involving azide intervention in the second step, is excluded.

We have made an examination of the catalysis by phenol of the reaction between triphenylmethyl chloride and tetra-*n*-butylammonium azide. We found, as expected, no definite order with respect to phenol. Though complex-formation cannot be excluded in principle, we have found no positive indication of the formation of a complex with the properties ascribed to it by Swain and Kreevoy. Both points may be illustrated by the longer of the sets of runs shown in Table 4, where we have a constant concentration of the azide throughout, and a rising concentration of phenol from run to run. As usual, we record initial specific rates $k_1°$.

TABLE 4. *Effect of added phenol on initial specific rate* ($k_1°$ *in sec.*$^{-1}$) *of consumption of triphenylmethyl chloride by reaction with tetra*-n-*butylammonium azide in benzene at* 30°.

[Initially, $[Ph_3CCl]_0 = 0{\cdot}05$M, throughout.]

Run	$[Bu_4NN_3]$	[PhOH]	$10^5k_1°$	Run	$[Bu_4NN_3]$	[PhOH]	$10^5k_1°$
Interpoln.	0·125	—	3·8	228	0·0125	0·025	225
226	,,	0·004	6·2	229	,,	0·050	670
227	,,	0·010	14·2	220, 222, 223	0·0500	—	12
231	,,	0·015	53·3	232	—	0·015	19

If we plot the logarithm of the excess rate due to phenol against the logarithm of the concentration of phenol, we obtain the curve shown in Fig. 3. Its slope varies continuously, showing no arrest at unity, or any other integral value within the range of the observations. If the kinetics were to be represented by Swain and Kreevoy's equation, then the rates must approximate to zero to the left of the vertical broken line in Fig. 3, where there would be no excess of azide over phenol.

With higher concentrations of tetra-*n*-butylammonium azide, the catalytic effect of phenol is generally similar but weaker. This may possibly be because, at the higher concentration of salt, higher multipolar aggregates, or more highly charged aggregates, of chemically active character, are formed by the salt, aggregates which the added phenol helps to break down, this retarding effect being superposed on the accelerating effect, which alone the phenol exerts at low concentrations of salt.

The short summary of these results on phenol catalysis is that, contrary to Swain and Kreevoy's statements, the catalysed reaction is not of third order, is not of first order in phenol, and, in fact, has no definite kinetic order in phenol. We conclude that there is no unique placing, such as is required by Swain's " push-pull " mechanism, of just one phenol molecule in the transition state of the catalysed substitution; and that the rôle of phenol is susceptible only of statistical description, as is implied in its classification as that of a co-solvent.

EXPERIMENTAL

Materials.—Their preparation is described in the preceding paper.

Kinetic Method.—The reaction mixtures were made up as usual (preceding paper), but to a total volume of 50 ml. Samples of 5 ml. were run into 5 ml. of redistilled aniline, which served as an efficient quenching medium, interrupting the reaction and liberating hydrogen chloride quantitatively from the triphenylmethyl chloride remaining in the sample. To this mixture, 20 ml. of 95% ethyl alcohol, containing bromothymol-blue, were added, and then a standard volume of 0·05N-sodium hydroxide in ethyl alcohol was added from an automatic pipette. This volume was 2 ml., 5 ml., or 7 ml., according as the initial concentration of triphenylmethyl chloride in the kinetic run had been 0·02, 0·05, or 0·07M. The solution was then titrated with 0·01N-hydrochloric acid in ethyl alcohol, to a colour standard. Two samples were withdrawn from each run as soon as possible after its commencement, and the mean time of withdrawal, and the mean of the analytical results obtained with the samples, were taken as defining the kinetic starting point. Formed triphenylmethyl azide was not affected by this procedure. Checks of the method were made without azide. The methods of calculation have been described, and typical results have been given, in the foregoing text.

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