

**238.** *Mechanism of Substitution at a Saturated Carbon Atom. Part LVI.\* Kinetics of the Reaction of Triphenylmethyl Chloride with Methyl Alcohol in Benzene.*

By E. D. HUGHES, C. K. INGOLD, (Miss) S. F. MOK, and Y. POCKER.

The methyl-alcoholysis of triphenylmethyl chloride in benzene has been reinvestigated. Swain reported measurements of the rate of this reaction in the presence of pyridine, asserting that pyridine does not react with the alkyl chloride and has no effect on the rate of its alcoholysis. It has been found that pyridine reacts relatively rapidly with triphenylmethyl chloride, and has a marked effect on the rate of its methyl-alcoholysis. The present investigation was therefore continued by the measurement of initial rates in the absence of pyridine.

Contrary to Swain's finding that the kinetic order is precisely two with respect to methyl alcohol, it is now found that this reaction has no definite order in that substance: the apparent order rises quite continuously from near zero to about three over our range of methyl alcohol concentrations, without any sign of an arrest at any intermediate value. Notwithstanding that methyl alcohol is the substituting agent, it appears to be exerting a macroscopic co-solvent effect on a rate-controlling step, and no evidence is forthcoming that two necessary and sufficient molecules have specific functions in the transition state, as is required by Swain's "push-pull" theory. A similar general co-solvent function is exerted by a number of added polar molecules, which are not acting as substituting agent: those investigated include the non-reacting aprotic molecules, nitromethane and nitrobenzene, and the slowly reacting hydroxylic molecule, phenol.

Swain claimed that the rate of alcoholysis is not depressed by common-ion salts (chlorides), and is not appreciably increased by non-common-ion salts. It is found, on the contrary, that tetra-*n*-butylammonium chloride markedly depresses the reaction rate. The functional form of the effect is in approximate agreement with the assumption that this is the "common-ion" effect in a reaction of  $S_N1$  type, *i.e.*, competitive intervention by the saline chloride in a product-controlling step, following a rate-governing step, of the reaction.

Hydrogen chloride is an electrophilic catalyst, apparently acting both through its molecules, and also through dissociated protons. Tetra-*n*-butylammonium perchlorate is a remarkably powerful catalyst, apparently acting through dissociated perchlorate ions. Other non-common-ion salts accelerate the reaction markedly, but less strongly than perchlorate: a reason for the quantitative difference is suggested. Added tetra-*n*-butylammonium chloride destroys the catalytic effect of hydrogen chloride by combining with it: protons are converted into hydrogen chloride molecules, and the latter are further converted into hydrogen-dichloride ions. Tetra-*n*-butylammonium chloride also destroys the catalytic effect of tetra-*n*-butylammonium perchlorate: the functional form of this effect is in accurate accord with the assumption that the saline chloride is again intervening, not in the first rate-controlling step, but in a product-controlling step of an  $S_N1$ -type mechanism.

SWAIN'S conclusion<sup>1,2</sup> that "there is only one mechanism for the displacement of anions," "always a push-pull termolecular mechanism," that "nucleophilic displacement reactions . . . are at least termolecular, never unimolecular or bimolecular," and that they have "exactly third order kinetics," unless solvent participation suppresses certain orders, inasmuch as "kinetics does not depend on mechanism, but only on the degree of

• Part LV, preceding paper.

<sup>1</sup> Swain, *J. Amer. Chem. Soc.*, 1948, **70**, 1119.

<sup>2</sup> Swain and Eddy, *ibid.*, p. 2989.

participation of the solvent," has been supported by several experimental reports, of which the most widely quoted is that on the reaction of triphenylmethyl chloride with methyl alcohol in benzene. It is claimed<sup>1,3</sup> that this process obeys a third-order rate law with precision, and that the positive normal, and negative, mass-law salt effects, which might be expected to appear if the unimolecular mechanism  $S_N1$  were in operation, are insignificant or absent.

In re-examining this subject, our first object was to check the kinetic facts: we found that they were not as reported. We then continued the investigation, because it became our object to see whether a more comprehensive survey of the kinetic pattern would appear consistent with either the  $S_N1$  or the  $S_N2$  mechanism of substitution, the concept of which, according to Swain, "has been popular" but is to be rejected as "false and misleading."<sup>4,5</sup>

(1) *The Experimental Conditions.*—They were our first difficulty. Swain's main series of data relate to the reaction of triphenylmethyl chloride (0.1M) with methyl alcohol (0.05 or 0.1M), sometimes with added phenol, but always with an added tertiary amine, usually pyridine in excess (0.1—0.2M), in a benzene solution saturated with, and containing in suspension, the hydrochloride of the amine. Swain does not suppose that such conditions are either needlessly, or dangerously, over-complicated. "The amine," he writes, is used simply to take up the hydrogen chloride formed and render the reaction irreversible. The reaction between trityl chloride and tertiary amines is negligibly slow under these conditions, and the rate of reaction with methanol is unaffected by changing the concentration of the tertiary amine used."

We do not confirm either of these findings. As to the first, we find that triphenylmethyl chloride reacts rapidly with tertiary amines, in particular, with pyridine. The reaction is reversible, but it goes forward extensively, and the forward rate is comparable with the rate of chlorine exchange of triphenylmethyl chloride with a saline radiochloride. a reaction which is generally faster than methyl-alcohololysis in like conditions, *e.g.*, 8 times faster in the presence of 0.1M-methyl alcohol in benzene (Part LIV). The time element can, as indicated in Part LIV, be studied conveniently by competition with chloride exchange; but the kinetics and thermodynamics of the reaction of triphenylmethyl chloride with pyridine are the subjects of a future paper, and we are concerned now only with the qualitatively greater rapidity of this reaction than of the reaction with methyl alcohol. The result of it is that, before the progress of the reaction with methyl alcohol comes to be measured, the faster reaction with pyridine has converted a certain proportion of the triphenylmethyl chloride into a form, which is not unreactive, but is less reactive than is the original material, towards methyl alcohol. And so, contrary to Swain's second finding, we observe that the rate of methyl-alcohololysis is reduced by added pyridine, and reduced the more by an increased concentration of pyridine. This is illustrated by the initial specific rates,  $k_1 = -d[RCl]/[RCl]dt$ , cited in Table 1.

TABLE 1. *Effect of added pyridine on the initial specific rate ( $k_1$  in sec.<sup>-1</sup>) of reaction of triphenyl chloride with methyl alcohol in benzene at 25°.*

(Initially, triphenylmethyl chloride was 0.1M, throughout.)							
Run	[MeOH] <sub>0</sub>	[Pyridine]	10 <sup>5</sup> k <sub>1</sub>	Run	[MeOH]	[Pyridine]	10 <sup>5</sup> k <sub>1</sub>
146	0.10	—	6.3	219	0.05	—	2.17
16	"	0.05	3.4	17	"	0.10	1.09
5	"	0.10	2.8	26	"	0.20	0.90
33	"	0.60	2.2	34	"	0.60	0.67

There is a slight quantitative exaggeration in this Table, inasmuch as the pyridine-free rates are rendered too high by the catalytic effect of adventitious hydrogen chloride. We know how to correct for this: and we know that, if the correction were made, it would

<sup>1</sup> Swain, *J. Amer. Chem. Soc.*, 1950, **72**, 2794.

<sup>4</sup> Swain and Langsdorf, *ibid.*, 1951, **73**, 2813.

<sup>5</sup> Swain and Moseley, *ibid.*, 1955, **77**, 3727.

not reduce the pyridine-free rates by more than 10%. This does not affect the conclusion that the rate is seriously disturbed by pyridine.

Since the findings on which Swain based the choice of his experimental conditions were not confirmed, it was evident that we could not continue to employ those conditions. A simplified procedure was required, and it was an obvious step to leave out the pyridine, and, of course, the pyridine hydrochloride, and to study initial rates. We expected that two new disturbances would arise in the continuing reaction, *viz.*, an autocatalytic acceleration, due to formed hydrogen chloride,<sup>6</sup> and a final retardation due to reversibility. However, by concentrating on initial rates, we could largely avoid disturbances. We soon found that a careful watch had to be kept on the effect, on initial rates, of adventitious hydrogen chloride. But this was a small problem compared with that of analysing the kinetics of two interacting, simultaneous, reversible reactions, both, as we now know, having inconstant reaction orders.

(2) *Order with Respect to Triphenylmethyl Chloride.*—In agreement with Swain,<sup>1</sup> we find that this kinetic order is unity. This is illustrated, in the first instance, by the initial specific rates,  $-d[\text{RCI}]/[\text{RCI}]dt$ , in Table 2, for two methyl alcohol concentrations. Here, the rate constants are uncorrected for catalysis by adventitious hydrogen chloride, but in these experiments the error so caused was only of the order of magnitude of the casual errors of the initial-rate measurements.

TABLE 2. *Effect of the concentration of triphenylmethyl chloride (RCI) on the initial specific rate ( $k_1$  in sec.<sup>-1</sup>) of its reaction with methyl alcohol at 25°.*

Run	[RCI] <sub>0</sub>	[MeOH] <sub>0</sub>	10 <sup>4</sup> k <sub>1</sub>	Run	[RCI] <sub>0</sub>	[MeOH] <sub>0</sub>	10 <sup>4</sup> k <sub>1</sub>
206	0.010	0.10	6.7	217	0.010	0.20	33
211 <i>d</i>	0.020	"	5.0	218	0.020	"	37
207	0.025	"	5.5	219	0.030	"	38
212	0.030	"	6.0	220	0.050	"	40
146	0.100	"	6.3	393	0.100	"	40

The test here illustrated is for a range 1 : 10 of triphenylmethyl chloride concentrations. We have enlarged the range to 1 : 40; but, with the higher concentrations of triphenylmethyl chloride, it is more difficult to keep down the adventitious hydrogen chloride, and it is easier to allow it to enter, but to correct for it. This further illustration must therefore wait until we go into the matter of hydrogen chloride catalysis (Section 4).

In the particular experiments to which Table 2 refers, we did not measure the equilibrium extent of reaction. But this is known approximately from many other measurements: when triphenylmethyl chloride and methyl alcohol are in equivalence, the reaction goes forward to the extent of about 11%, but when either reagent is in excess over the other, then the consumption of that in deficit proceeds much further, *e.g.*, to more than 80%.

(3) *"Order" with Respect to Methyl Alcohol.*—According to Swain, the reaction between triphenylmethyl chloride and methyl alcohol, besides being of first order in triphenylmethyl chloride, is of second order in methyl alcohol, and so of third order overall, these orders holding with great accuracy: "The fact that the order is so precisely third," he says, "suggests that we are dealing with a pure mechanism, which accounts for all the reaction observed."<sup>1</sup>

Our data on the dependence of the rate on methyl alcohol concentration are in Table 3. The concentration range is 1 : 250, with the accuracy falling off at both extremes, but with a similar degree of accuracy over a central range of 1 : 80. The rates are again uncorrected for catalysis by adventitious hydrogen chloride, but the correction that some of the figures need on this account is not more than twice the casual error, and is of no significance in a range of rates of 1 : 1000. It happens that the equilibrium extent of reaction was measured in many of these experiments, and so we take the opportunity to illustrate this matter in Table 3.

Bateman, Cooper, and Hughes, *J.*, 1940, 930 (electrophilic catalysis by HCl of alkyl chloride reactions in aprotic solvents); Part LIII, Hughes, Ingold, Patai, and Pocker, *J.*, 1957, 1206 (stability of ClHCl<sup>-</sup> ion in benzene, the reason for the catalysis).

TABLE 3. *Effect of the concentration of methyl alcohol on the initial specific rate ( $k_1$  in sec.<sup>-1</sup>) of its reaction with triphenylmethyl chloride (RCI) in benzene at 25° ([RCI]<sub>0</sub> = 0.1M).*

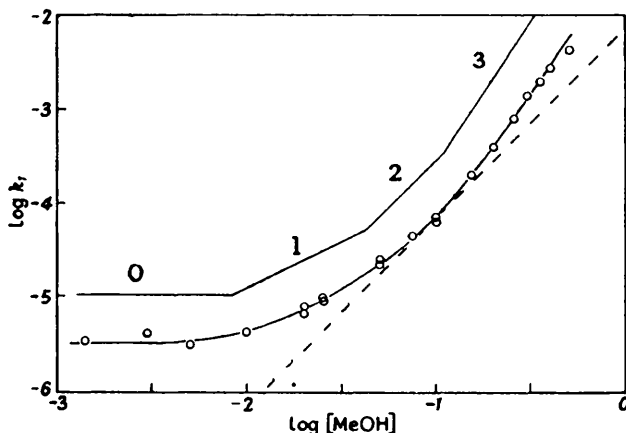
Run	[MeOH]	10 <sup>4</sup> k <sub>1</sub>	MeOH (%) *	Run	[MeOH]	10 <sup>4</sup> k <sub>1</sub>	MeOH (%) *
250	0.002	~0.35	85.0	131	0.075	4.5	12.0
253	0.003	~0.42	60.0	146	0.100	6.3	10.5
249	0.005	0.30	42.0	130	"	7.0	11.0
248	0.010	0.42	32.0	156	"	7.3	11.0
132	"	0.43	—				
410	0.020	0.65	—				RCI (%) *
370	"	0.82	—	133	0.150	20	15.0
251	0.025	0.85	—	393	0.200	40	—
128	"	1.00	19.5	134	0.250	83	21.5
129	0.050	2.2	15.0	432	0.300	137	—
15d	"	2.3	14.5	10	"	140	26.0
252	"	2.5	—	135	0.350	200	29.0
291	"	2.6	—	136	0.400	270	32.5
359	"	2.6	—	137	0.500	~430	39.0

\* Consumed at equilibrium.

The meaning of Table 3 is best indicated by plotting the logarithm of the first-order rate-constant in triphenylmethyl chloride against the logarithm of the concentration of methyl alcohol, as in Fig. 1. According to Swain, it should be a straight line of slope 2. The curve as drawn shows every slope from 0 to 3, and there is no arrest of gradient at 2

FIG. 1. *Reaction of triphenylmethyl chloride with methyl alcohol in benzene at 25°: plot of the logarithm of the first-order rate constant with respect to triphenylmethyl chloride against the logarithm of the concentration of methyl alcohol.*

The upper series of straight lines shows theoretical slopes for kinetic orders of 0, 1, 2, 3, with respect to methyl alcohol. The broken line represents Swain's view of the kinetics of this reaction, the kinetics required by the "push-pull termolecular" theory.



or any other integral value within the range. We cannot be quite sure that the represented arrest at 0 is real, because our experiments at low concentrations of methyl alcohol are not accurate enough.

The description given by Swain of the kinetics of this reaction is therefore incorrect in its most fundamental point. It follows that his conclusions cannot be sustained. There cannot be a small, necessary, and sufficient number, two or any other, of methyl alcohol molecules, singularly placed, with distinctive functions, in the transition state of the rate-controlling step of this reaction. Certainly, methyl alcohol is the nucleophilic substituting agent. But the kinetic evidence is that its participation in the rate-controlling stage of substitution is of the nature of that of a polar co-solvent, the molecules acting in an electrostatic way, in various numbers, from various positions, not necessarily very close to the reaction centre, and in a manner that could not be accurately described, otherwise than statistically. It follows that Swain's simple "push-pull" diagram has no sound factual basis.

Swain and Kreevoy have complained <sup>7</sup> that one of us "reclassified" the reaction of triphenylmethyl chloride with methyl alcohol in benzene as an S<sub>N</sub>2 process. But that was accepting Swain's reported facts; and what was said <sup>8</sup> was that they allow that

<sup>7</sup> Swain and Kreevoy, *J. Amer. Chem. Soc.*, 1955, **77**, 1122.

<sup>8</sup> Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell & Son, London, 1953, p. 356.

interpretation, as indeed they do. The present observations do not allow it. Hawthorne and Cram<sup>9</sup> have similarly disagreed with what they call "the experimentally unsupported viewpoint of Hughes" that the reaction is of  $S_N2$  type. Actually the viewpoint was not experimentally unsupported: it was insecurely supported by Swain's experiments which we have now shown to be inaccurate. No comparison of absolute rates with Swain's values is possible because of the complications arising from the bases he added.

As this reaction has no invariable reaction-order, an activation energy, as determined from the temperature coefficient of reaction rate, would have no clear meaning. It is, however, convenient for the purpose of comparing the absolute rates of different reactions of triphenylmethyl chloride, not all of them measured at the same temperature, to have an idea of the experimental temperature coefficient of the rate of reaction with methyl alcohol. We have estimated this roughly for the methyl alcohol concentration 0.05M, by rate measurements at 25°, 35°, and 45°, and find the factor of increase for 10° rise in temperature to be close to 1.6.

Hudson and Saville<sup>10</sup> investigated the ethyl-alcoholysis of triphenylmethyl chloride in solvent carbon tetrachloride, in the range 0.1—5M-ethyl alcohol. Their logarithmic plot, corresponding to that of Fig. 1, showed slopes varying continuously, but non-monotonically, from below 2 to about 3. Where their concentration range and ours overlap, the slopes are not widely different, though neither is constant. They suggest that the active agent is a trimer of ethyl alcohol, but we find it difficult to believe that a probably cyclic trimer, in such relatively low concentration as would give an approximately cubic rate-law, would be more effective in reaction than the monomer.

(4) *Catalysis by Hydrogen Chloride.*—The difficulty of this subject is that there are really two catalyses, one of which would be very easy to miss. There is one of moderate power at measurable hydrogen chloride concentrations, and also one of great specific power at concentrations too small for accurate measurement. For convenience we call them the "measurable" and the "immeasurable" catalysis. The difficulty of the diagnosis is this: if one determines reaction rate for a series of concentrations of hydrogen chloride, down to the lowest that one can measure with some attempt at precision, say  $5 \times 10^{-4}$ M, and if one then extrapolates down to zero concentration, in order to get the acid-free rate, the answer is wrong, with nothing in the work to indicate that it might be wrong. Obviously we cannot check the acid-free rate directly, because, however early one makes one's measurements of the initial rate, one must allow a measurable amount of acid to develop. Moreover, we have never succeeded in reducing the adventitious acid in, say, a 0.1M-solution of triphenylmethyl chloride, with all manipulations made in readiness

TABLE 4. Effect of hydrogen chloride on the initial specific rate ( $k_1$  in sec.<sup>-1</sup>) of reaction of triphenylmethyl chloride (RCI) with methyl alcohol in benzene at 25°.

(Initially, [MeOH] = 0.1M throughout. As far as possible, the value of  $h = [HCl]$  is taken as that at the centre of the small concentration range covered by the group of initial measurements from which the initial rate was determined.)

Run	[RCI] <sub>0</sub>	10%h	10% $k_1$	Equil. (%) <sup>*</sup>	Run	[RCI] <sub>0</sub>	10%h	10% $k_1$	Equil. (%) <sup>*</sup>
—	—	0	7.0†	—	108	0.3	32.0	15.7	—
92	0.1	6.2	8.3	10.6	123	0.1	37.3	13.4	9.0
115	„	14.0	10.0	10.2	112	„	47.0	19.5	9.0
12	„	15.0	10.3	—	110	0.4	60.0	20.7	—
106	0.2	16.0	11.7	9.5	114	0.1	87.0	25.8	8.0
122	0.1	23.3	12.7	—	121	„	117.5	34.0	7.0

\* Percentage of methyl alcohol consumed at equilibrium.

† Value by extrapolation: not the true value.

for a run, to less than an estimated  $2 \times 10^{-5}$ M, so that all our runs started acid, besides becoming more acid during the measurements.

The measurable catalysis is easily documented. Table 4 does this, and also takes

<sup>9</sup> Hawthorne and Cram, *J. Amer. Chem. Soc.*, 1954, **76**, 3451.

<sup>10</sup> Hudson and Saville, *J.*, 1955, 4130.

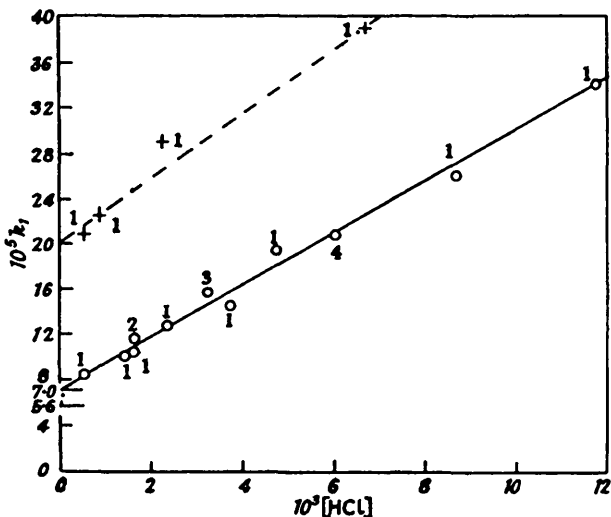
care of two further points. One, promised in Section 2, is that the reaction is of first order in triphenylmethyl chloride, not only from 0.01 to 0.10M, but also over the extension of range to 0.40M. The other is that added hydrogen chloride represses the reaction equilibrium in the direction of the factors, as would be expected qualitatively, since hydrogen chloride is a product of the reaction.

The form of the catalysis is shown in Fig. 2: it is linear: and points representing experiments with from 0.1M- to 0.4M-triphenylmethyl chloride lie about the same line. Here we have an apparently real reaction order, one of unity in hydrogen chloride. The rate term is of the form  $k'h$ , the catalytic coefficient  $k'$  having the value  $0.023 \text{ sec.}^{-1} \text{ mole}^{-1}$  l. in 0.1M-methyl alcohol in benzene at  $25^\circ$ ;  $h$  is the concentration of hydrogen chloride.

We assume that the hydrogen chloride molecule is functioning here as a catalyst of the specific electrophilic type, discussed as to principle in 1940, and that it owes its power

FIG. 2. The full-line curve represents the effect of hydrogen chloride on the initial specific rate of reaction of triphenylmethyl chloride with methyl alcohol in benzene at  $25^\circ$ .

According as the points are numbered 1, 2, 3, 4, the concentration of triphenylmethyl chloride was 0.1, 0.2, 0.3, 0.4M. The concentration of methyl alcohol was 0.1M throughout. The non-linear extrapolation (broken) on the extreme left of the lower (full) curve is referred to later in this Section. The linear broken curve, representing experiments in the presence of 0.001M-tetra-*n*-butylammonium perchlorate, is referred to in Section 6.



to the stability of the  $(\text{ClHCl})^-$  ion in benzene.<sup>6</sup> The kinetic law shows that it is specific, *i.e.*, that, unlike methyl alcohol, hydrogen chloride does accept a specific placing of a small number of its molecules, one, in fact, in the transition state of catalysed reaction.

Before we can consider the "immeasurable" catalysis, it is necessary to notice the effect of tetra-*n*-butylammonium chloride in suppressing the measurable catalysis by hydrogen chloride. We know that chloride ion combines with hydrogen chloride to give the hydrogen-dichloride ion: therefore we must expect a suppression of the catalysis. The figures in Table 5 show that a quantity of salt equivalent to the hydrogen chloride destroys

TABLE 5. *Suppression by tetra-*n*-butylammonium chloride of the catalysis by hydrogen chloride of the reaction of triphenylmethyl chloride with methyl alcohol in benzene at  $25^\circ$ .*

[Triphenylmethyl chloride and methyl alcohol are each in concentration 0.1M throughout. Initial specific rates  $k_1$  are in  $\text{sec.}^{-1}$ .]

Run	$10^4 h$	$[\text{Bu}_4\text{NCl}]$	$10^5 k_1$	Run	$10^4 h$	$[\text{Bu}_4\text{NCl}]$	$10^5 k_1$
Fig. 2	76	—	25.5	Fig. 2	13	—	10.0
279	"	0.0010	23.8	276	"	0.0199	4.3
278	"	0.0070	14.0	Fig. 2	0	—	7.0
277	"	0.0199	4.7	275	"	0.0199	4.3

much of the catalytic effect of the latter, and that three times as much salt more than suffices to destroy the whole of it. (Actually, at the highest concentration shown in Table 5, the salt is not only suppressing all the forms of hydrogen chloride catalysis, but is also beginning to exert its own specific power of retarding the reaction.)

Knowing that it requires an amount of tetra-*n*-butylammonium chloride in excess of the amount of hydrogen chloride to suppress nearly all the measurable catalysis of the

latter, we can estimate about how much salt should be needed to suppress this catalysis at the lowest concentrations that can be determined, in association with a measured rate, say,  $5 \times 10^{-4}\text{M}$  for experiments with triphenylmethyl chloride and methyl alcohol both  $0.1\text{M}$ . We can also estimate, from the form of this catalysis, what the rate should be in its absence. Thus, for the conditions represented by the first point in Fig. 2, we can say that the required amount of salt would be about  $10^{-3}\text{M}$ , and that it should depress the rate to  $7.0 \times 10^{-5} \text{ sec.}^{-1}$ . Our evidence for a second catalytic effect of hydrogen chloride, the "immeasurable" effect, is that an amount of salt 1000 times smaller depresses the rate more than that, and that rate depressions produced by such very small concentrations of salt reach their limit well below the concentrations which begin to produce a noticeable effect on the measurable catalysis.

Numerical illustration of this effect involves the difficulty of standardising, among different experiments, the smallest amount of hydrogen chloride that can be associated with what can fairly be called initial rates. With the reagents at  $0.1\text{M}$ -concentration, and no salt present, one can, if one pays no attention to this condition, observe various initial rates between  $6 \times 10^{-5}$  and  $9 \times 10^{-5} \text{ sec.}^{-1}$ . The most comparable collection of experiments we have involve adventitious-plus-developed acid amounting to about  $5 \times 10^{-4}\text{M}$  over the period of the readings. These results are summarised in Table 6.

TABLE 6. Effect of small concentrations of tetra-*n*-butylammonium chloride on the rate of reaction of triphenylmethyl chloride with methyl alcohol in benzene at  $25^\circ$ .

(Initially,  $[\text{CPh}_3\text{Cl}] = [\text{MeOH}] = 0.1\text{M}$ . In the period of the readings, the hydrogen chloride concentration  $h$  averaged  $5 \times 10^{-4}\text{M}$  throughout. Initial specific rates,  $k_1$ , are in  $\text{sec.}^{-1}$ .)

Run	$10^4[\text{Bu}^n_4\text{NCl}]$	$10^4k_1$	Run	$10^4[\text{Bu}^n_4\text{NCl}]$	$10^4k_1$
92	—	8.3	223	28	5.7
296, 301	1.07	6.4	300	107	5.5
230, 299	12.3	6.0	142d, 224, 228	240	5.7

The form of this rate depression is shown in Fig. 3. The effect is all over by the time the salt concentration has amounted to  $3.0 \times 10^{-5}\text{M}$ . The rate is then  $5.6 \times 10^{-5} \text{ sec.}^{-1}$ , and there it remains until the salt concentration is increased a great deal further. Unfortunately we cannot analyse the curve mathematically, because the acid concentration cannot be specified with sufficient precision. If we could analyse it, we would hope to prove what must now be put forward as a speculation.

It has already been made clear that the linear curve in Fig. 2 ought not to be extrapolated linearly: the true curve must turn down very close to the rate axis, somewhat as indicated by the added broken curve. Now the experimentally followed, straight curve represents a rate-term  $k'h$ , where  $h$  is the concentration of hydrogen chloride. That the true curve turns down at the end of low concentration indicates the presence of another rate-term with a smaller exponent than unity, *i.e.*, a term representing a specifically more powerful catalysis, but one of smaller kinetic order. We assume that this order, definitely less than 1, is  $\frac{1}{2}$ , *i.e.*, that the new rate term is of the form  $k''h^{\frac{1}{2}}$ , and that it is due to electrophilic catalysis by the protons of dissociated hydrogen chloride.

From the viewpoint of dissociation to simple ions in benzene, even quaternary ammonium salts are very weak electrolytes: they are dissociated by some millionths at most to give concentrations of ions which cannot be increased much above  $10^{-10}\text{M}$ . But however weak salts are, hydrogen chloride must be a much weaker electrolyte. Whether we assume that it is 100 times or 10,000 times weaker, it will be true that a quaternary ammonium chloride, added in considerably smaller concentration than the hydrogen chloride, will practically completely repress dissociation of the latter. We shall later illustrate the point that a chloride is needed, *i.e.*, that any quaternary ammonium salt will not act thus (Section 6).

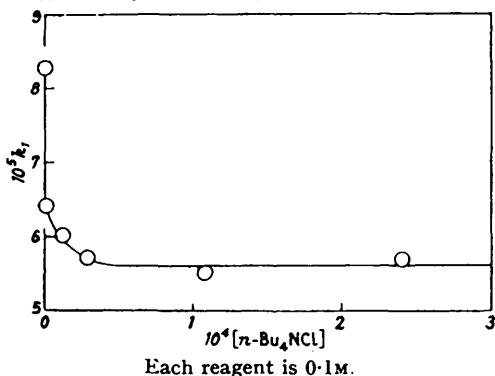
We have done similar experiments at lower methyl alcohol concentrations, down to  $0.02\text{M}$ . The rate phenomena are of the general form shown in Fig. 3, except that the initial fall of rate is even sharper, and that at the methyl alcohol concentration  $0.02\text{M}$ , the

horizontal stretch of curve becomes replaced by a curve with a small, but distinct, initial rise, so that it leaves a shallow minimum, and only asymptotically attains horizontality. The steepening of the initial rate fall suggests that the removal of methyl alcohol weakens hydrogen chloride, as a simple binary electrolyte, more than it weakens the quaternary ammonium salt. We have a suggestion to account for the small rise of rate, but must postpone making it until salt effects in general have been considered more thoroughly (Section 6).

(5) *Kinetic Effect of Tetra-n-butylammonium Chloride.*—In his first paper<sup>1</sup> on the reaction now under consideration, Swain reported that ammonium chlorides showed no negative kinetic effects, such as might have indicated a unimolecular mechanism  $S_N1$ : "There is no indication of a mass effect, *i.e.*, a reversal of carbonium ion formation caused by chloride ion." In a later paper he reaffirmed this finding.<sup>3</sup>

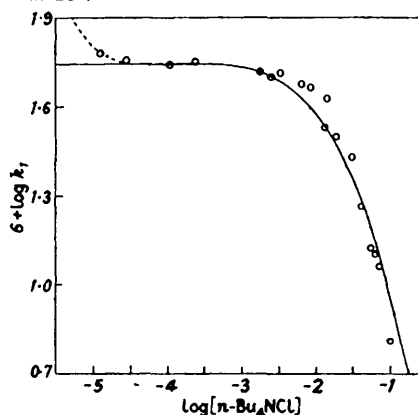
We do find a negative kinetic effect: with tetra-*n*-butylammonium chloride, it becomes noticeable at all concentrations above  $10^{-3}M$ . By the time the added salt has

FIG. 3. Effect of low concentrations of tetra-*n*-butylammonium chloride on the initial specific rate of reaction of triphenylmethyl chloride with methyl alcohol at 25° in benzene.



Each reagent is 0.1M.

FIG. 4. Logarithmic plot showing the effect of moderate and high concentrations of tetra-*n*-butylammonium chloride on the initial specific rate of reaction of triphenylmethyl chloride with methyl alcohol in benzene at 25°.



Each reagent is 0.1M.

become equivalent to the methyl alcohol, the rate may have fallen to one-eighth or less of its original value. This is illustrated in Table 7. The Table also shows, though in a somewhat qualitative way, that the added salt so shifts the equilibrium that the forward reaction goes further: some of the runs were followed for most of the distance they would go, and this is recorded, though the experiments were not continued for long enough to ensure that these extents of followed reaction represent equilibrium compositions.

TABLE 7. Effect of moderate and large concentrations (*c*) of tetra-*n*-butylammonium chloride on the initial specific rate ( $k_1$  in  $sec^{-1}$ ) of reaction of triphenylmethyl chloride (0.1M) with methyl alcohol (0.1M) in benzene at 25°.

Run	$10^3c$	$10^5k_1$	Followed % *	Run	$10^3c$	$10^5k_1$	Followed % *
Section 4	—	5.6	—	148	19.0	3.17	—
150	1.77	5.2	12	152	31.3	2.67	31
14	2.50	5.0	10	149	39.6	1.83	44
145	3.41	5.2	13	153	50.9	1.32	—
144	6.81	4.8	15	154	59.6	1.27	—
151	8.80	4.7	—	157	69.7	1.15	—
143	13.6	3.4	19	158	98.1	0.65	—
147	16.5	4.3	—				

\* Of the stoichiometric maximum: the thermodynamic maxima are not much higher than the figures recorded.



The functional form of this effect is shown in Fig. 4 : in order to cover a great range of concentrations, we have made the plot one of the logarithm of the rate against the logarithm of the concentration of salt. When the salt is added in increasing amounts, the first thing it does is to destroy all catalysis by hydrogen chloride : the tail-end of that process is seen on the left. After that, nothing happens until the concentration of salt becomes a multiple percentage of that of the methyl alcohol, then the rate curve plunges downward, as seen on the right.

The curve actually drawn is not the best curve through the points, but that given by the simplest conceivably applicable form of the theory of common-ion retardation in the unimolecular mechanism  $S_N1$ . This is that the preliminary step is a rate-controlling ionisation of the alkyl halide  $RCl$ , and that the formed carbonium ion  $R^+$ , which in our case might be in the ion-pair form  $R^+Cl^-$  (we are not required to reach a decision on the point at this stage), is rapidly attacked by the added salt in ion-pair form, and by methyl alcohol, in competition. If we assume that the salt is present almost wholly as ion-pairs, that the mass-law is obeyed, and that no other kinetic effect complicates this situation, the equation representing the kinetic effect is :

$$k_1^c = k_1^0 / \{1 + \alpha c/m\}$$

where  $c$  is the concentration of salt,  $m$  is that of methyl alcohol,  $k_1^c$  is the first-order rate-constant in the presence of the salt, and  $k_1^0$  that in its absence, whilst  $\alpha$  is the factor which expresses by how many times the specific rate of carbonium ion capture by salt is greater than the specific rate of its capture by methyl alcohol. In drawing the curve shown, this ratio  $\alpha$  has been taken as 5.

Some systematic disagreement is obvious : the points near  $c = 10^{-2}$  lie too high, and those near  $c = 10^{-1}$  too low. Since  $\alpha$  is adjustable, the real discrepancy might lie in only one of these regions, for we could obviously choose  $\alpha$  to reduce either discrepancy at the expense of the other. On the other hand, the curve might be about rightly drawn as it is. For quadrupoles are likely to be less effective than ion-pairs, whilst negatively charged ionic aggregates are likely to be more effective when they can arise in more than minute proportions. From Kraus and Fuoss's work (and partly from our own), we know that quadrupoles accumulate at the expense of pairs towards  $c = 10^{-2}$ , and that charged higher aggregates arise in considerable quantity towards  $c = 10^{-1}$ . Thus our rates might well deviate from a curve which is calculated on the assumption that the salt is in a single electrolytic form by being too high near  $c = 10^{-2}$  and too low near  $c = 10^{-1}$ , because of these known changes in the electrolytic situation with changing salt concentration.

(6) *Kinetic Effect of Other Tetra-n-butylammonium Salts, especially the Perchlorate.*— In emphasising the alleged absence, in the methyl-alcoholysis of triphenylmethyl chloride, of a mass-law retardation by adding saline chlorides, Swain remarked<sup>1</sup> : "It is true there is a positive salt effect, but it is of small magnitude." Actually, the few figures given do not all support this statement. However, some time later, when resisting a suggestion by Hine that, in accepting chlorides (which would be common-ion salts in an  $S_N1$  mechanism) as suitable for testing for a positive salt-effect, Swain was taking for granted what was to be proved, the latter author examined the kinetic influence of some added tertiary ammonium sulphonates, and reported that their effect on the rate was negligible.

The over-riding objection to these experiments is that the presence of pyridine vitiates all studies of salt-effects. But even without pyridine, there would be an objection to the use of sulphonates, and it applies equally to several other classes of salt, *e.g.*, nitrates or iodides : triphenylmethyl sulphonates, nitrates, iodides, etc., probably, if not certainly, exist in covalent form. Hence the first effect of the salt might be to divert a part of the triphenylmethyl chloride from its reaction with methyl alcohol, towards reaction with the salt to give triphenylmethyl sulphonate, etc., which would subsequently enter into reaction with methyl alcohol, but at less than its normal rate, because what was intended as a non-



methyl alcohol concentrations, catalyses by the salt and by hydrogen chloride are independent, and in a rough sense additive. This is illustrated by the rates in Table 10A, which apply to a fixed salt concentration with various amounts of adventitious-plus-introduced hydrogen chloride. Plotted in Fig. 2, these points lie about a linear curve nearly parallel to the salt-free curve for catalysis by hydrogen chloride, and displaced above it by nearly the rate-increase due to the salt in hydrogen-chloride-free conditions. At low methyl alcohol concentrations, there is an interaction between the two catalyses, as illustrated in Table 10B, to which we shall refer later. But our first object will be to

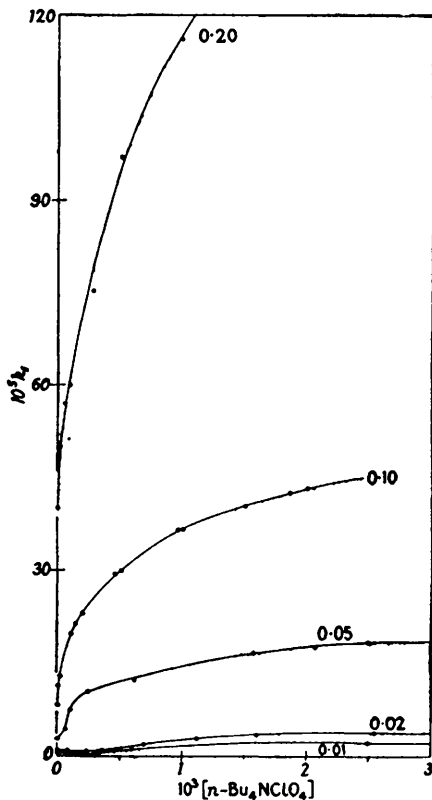


FIG. 5. Effect of tetra-*n*-butylammonium perchlorate (in concentration  $p$ ) on the initial specific rate ( $k_1$ ) of reaction of triphenylmethyl chloride on methyl alcohol in benzene at 25°.

The concentration of triphenylmethyl chloride was 0.1M throughout. The concentrations (M) of methyl alcohol are indicated by the figures against the curves.

interpret the obviously simpler situation applying to the higher methyl alcohol concentrations, and for this purpose it is clear that the salt-free rate must be taken as the directly determined rate without the salt, even though this rate includes a small catalytic contribution from the hydrogen chloride.

In order to extract a meaning from the relations illustrated in Fig. 5, we replot them as far as possible in the form  $\log(k_1^p - k_1^0)$  versus  $\log p$ , where  $k_1^p$  is the specific rate in the presence of a concentration  $p$  of salt, and  $k_1^0$  is the salt-free rate discussed above. We can do this for those curves for which  $k_1^p - k_1^0$  is everywhere positive, *i.e.*, for the methyl alcohol concentrations 0.3, 0.2, 0.1, and 0.05M. The result is in Fig. 6. There, the straight lines are all drawn to have a slope of  $\frac{1}{2}$ . We see that, for 0.3M-, 0.2M-, and 0.1M-methyl alcohol, the data agree with these lines over long ranges, though the experiments with 0.1M-methyl alcohol show diminished catalysis at the high-concentration end of the full experimental range, and the experiments with 0.05M-methyl alcohol agree with the drawn line in only a very imperfect way, inasmuch as there is reduced catalysis at both ends of the experimental range.

This is a central point in our interpretation of tetra-*n*-butylammonium perchlorate catalysis, as we prefer to call it, since the term "salt effect" has been so much linked with

TABLE 10. *Joint catalysis by tetra-*n*-butylammonium perchlorate and hydrogen chloride of the reaction of triphenylmethyl chloride with methyl alcohol in benzene at 25°.*(A) [Triphenylmethyl chloride and methyl alcohol each 0.1M, and tetra-*n*-butylammonium perchlorate 0.001M, throughout. Initial specific rates  $k_1$  are in sec.<sup>-1</sup>.]

Run	HCl	$10^5 k_1$	Run	HCl	$10^5 k_1$
271	0.0005	20.8	273	0.0023	27.0
272	0.0008	22.5	274	0.0067	39.2

(B) [In the following runs, triphenylmethyl chloride is 0.1M, methyl alcohol 0.02M, and hydrogen chloride 0.001M; the concentration of tetra-*n*-butylammonium perchlorate is varied. For comparison, interpolated values from Table 9 are given, corresponding to the hydrogen chloride concentration 0.0005M, all other concentrations being the same. Initial specific rates  $k_1$  are in sec.<sup>-1</sup>.]

Run	[Bu <sub>4</sub> NClO <sub>4</sub> ]	$10^5 k_1$ (HCl = 0.001M)	$10^5 k_1$ (HCl = 0.0005M)	$\Delta(10^5 k_1)$ for $\Delta\text{HCl} = 0.0005\text{M}$
415	—	1.0	0.8	0.2
418	0.00074	2.5	2.2	0.3
419	0.00174	7.0	3.3	3.7
420	0.00262	8.2	4.0	4.2

the ionic-atmosphere concept, which is inapplicable to solvent benzene: we have found that the catalysis has a limiting kinetic order of  $\frac{1}{2}$ . This kinetic "square-root law" is better obeyed in the higher methyl alcohol concentrations, but even there it is not generally obeyed for salt concentrations above  $10^{-3}\text{M}$ . Now we know that at all concentrations up to  $10^{-3}\text{M}$ , but not necessarily much above that value, nearly all the salt is present as ion-pairs. Therefore the evident meaning of our square-root relation is that one simple ion only of the salt is involved in the transition state of the reaction. We can go further and say that ion-pairs as such are not involved, even though they are so plentiful, nor are higher aggregates, over the range in which the square-root law is obeyed. Because different tetra-*n*-butylammonium salts behave so differently, there can be no doubt that the one simple ion of the perchlorate which is active is the perchlorate ion, not the tetra-*n*-butylammonium ion.

The kinetic deviations found at high salt concentrations may be ascribed to the considerable formation of higher aggregates than ion-pairs: for example, if, in the presence of such aggregates, the one active species were still the simple perchlorate ion, then the slope of the logarithmic plot should, as pairs became replaced by quadrupoles, fall from  $\frac{1}{2}$  to  $\frac{1}{4}$ . This type of deviation seems not to set in quite so early at the highest methyl alcohol concentrations used, and it may be that, in these concentrations, the methyl alcohol is beginning to be effective in resisting the formation of ionic aggregates higher than pairs.

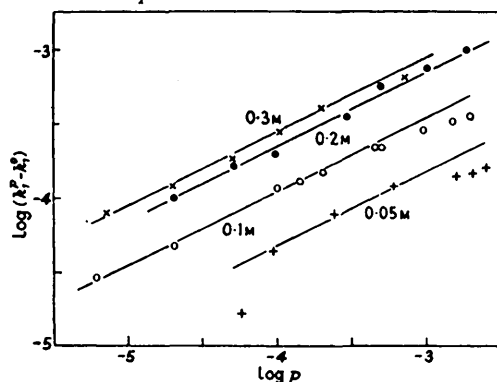
There remain for consideration the deviations which arise when the methyl alcohol concentration and the salt concentration are both low. These effects, which are retarding, first become quantitatively apparent at the methyl alcohol concentration 0.05M. They develop into a qualitatively noticeable negative catalysis at the still lower methyl alcohol concentrations 0.02M and 0.01M. As the salt concentration is built up, all these anti-catalytic tendencies or effects disappear, giving place to the usual positive catalysis.

In order to understand this, we must go back to the two hydrogen chloride catalyses, and, in particular, to what we called the "immeasurable" catalysis, which could be destroyed with very minute amounts of an ammonium chloride. Our interpretation was that this catalysis was due to simple protons, extremely active, but present in very small concentrations, so that they could be destroyed by very small amounts of a saline chloride. The basic reason why they could be so destroyed is because hydrogen chloride is a very weak acid in the benzene media, and, in particular, is weaker as an acid than the saline chloride is weak as a salt (weak though that is). A simple extension of this interpretation will allow us to understand all the low-concentration kinetic effects described above. What we have to assume is that, whilst in 0.3M-, 0.2M-, and 0.1M-methyl alcohol in benzene, perchloric acid is too strong an acid to allow an added saline perchlorate to take up the free protons, in 0.05M-methyl alcohol, it is not quite strong enough to confer on protons

so complete an immunity against the salt, and in 0.02M- and 0.01M-methyl alcohol it has become so weak as an acid, relatively to the weakness of the saline perchlorate as a salt, that a moderate amount of the saline perchlorate (though more than would have been needed of a chloride) is able to take up the free protons. This is the first effect that we observe on adding tetra-*n*-butylammonium perchlorate progressively at these low methyl alcohol concentrations: it amounts to a destruction of the "immeasurable" (protonic) part of the hydrogen chloride catalysis. A saline perchlorate cannot destroy the measurable (molecular) part of the hydrogen chloride catalysis, because the anion  $\text{ClHClO}_4^-$  does not exist (Part LIII). Therefore, once the "immeasurable" acid catalysis has been dealt with, the salt becomes free to exert its own catalytic effect.

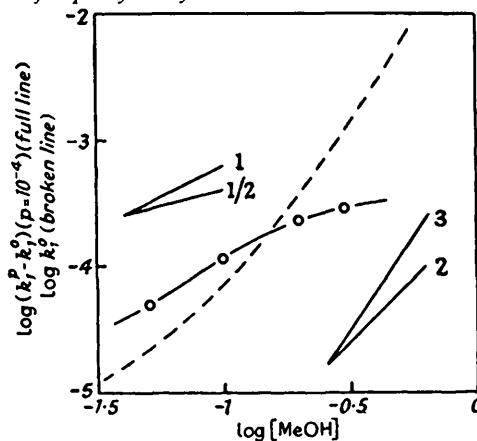
We can summarise this explanation by saying that, whilst at high methyl alcohol

FIG. 6. Plot of logarithm of the catalysed rate of reaction of triphenylmethyl chloride with methyl alcohol in benzene at 25° against the logarithm of the concentration of the catalyst, tetra-*n*-butylammonium perchlorate.



The straight lines, drawn with a slope of  $\frac{1}{2}$ , show that this catalysis has a limiting kinetic order of  $\frac{1}{2}$  with respect to the salt. The different lines, each with its set of points, relate to the different methyl alcohol concentrations (M) entered against the lines.

FIG. 7. Effect of methyl alcohol concentration on the rate of perchlorate-catalysed methyl-alcoholysis of triphenylmethyl chloride in benzene at 25°.



The continuous curve is a plot of the logarithm of the excess rate, given by the addition of a constant concentration ( $10^{-4}\text{M}$ ) of tetra-*n*-butylammonium perchlorate, versus the logarithm of the concentration of methyl alcohol. The broken curve is a corresponding plot for the rate of reaction in the absence of the salt. The catalysed reaction is evidently less kinetically sensitive to methyl alcohol, than is the uncatalysed reaction. The short straight lines show the slopes which would represent various simple kinetic orders in methyl alcohol.

concentrations, perchlorate catalysis is non-interacting with hydrogen chloride catalysis, at low concentrations of methyl alcohol, the perchlorate and hydrogen chloride catalyses interact. That there is a general interaction between the two forms of catalysis at low concentrations of methyl alcohol, has already been illustrated in Table 10B.

We can now make the suggestion which is needed to complete our interpretation of the rate curves obtained for the progressive addition of tetra-*n*-butylammonium chloride (Sections 4 and 5). What was left incomplete was the explanation of an extra feature which these curves show at low methyl alcohol concentrations. We then observe, as the salt is progressively added, first, a sharp fall of rate (destruction of both forms of hydrogen chloride catalysis), then a small rise (the unexplained additional feature), then no effect (horizontal stretch of curve), and finally a strong fall (common-ion retardation). We think that the small rise is due to catalysis by the  $\text{ClHCl}^-$  ion, produced by addition of chloride ion to the adventitious hydrogen chloride. This ion must be the anion of a very strong acid (since  $\text{H}_2\text{Cl}_2$  seems not to exist as such), and, in media in which the anion is

stable enough not to come to pieces in the process, it might act like a perchlorate ion in the transition state of the reaction under consideration. We are here assuming that the anion, which is stable in benzene but unstable in water, becomes more stable as we remove hydroxylic material, such as methyl alcohol, from the benzene solution.

Our data, and in particular the representation given in Fig. 6, provide a basis for considering the effect of methyl alcohol concentration on the rate of perchlorate-catalysed methyl-alcoholysis. If we draw a vertical line anywhere in Fig. 6, within the range of salt concentration in which the square-root law is obeyed, say, at  $p = 10^{-4}M$ , the catalysed rates, that can be read off from the produced intersections, may be plotted against the relevant concentrations of methyl alcohol. By "catalysed rate," we mean, of course, the excess of the total rate over what the rate would be were the salt omitted. This plot is given in Fig. 7 as a graph of the logarithm of the catalysed rate *versus* the logarithm of the methyl alcohol concentration. If we should take a different perchlorate concentration, still within the range of validity of the square-root law, the curve in Fig. 7 would simply be shifted vertically. Thus the gradient of this curve at any point represents the formal kinetic order of the catalysed reaction with respect to methyl alcohol at that concentration of methyl alcohol. One sees that, as for salt-free methyl-alcoholysis, the kinetic order in methyl alcohol of the catalysed reaction is indefinite. It is also somewhat small, varying between about one-half and one. For comparison, the analogous logarithmic plot for the uncatalysed reaction is reproduced in Fig. 7. In this, the formal kinetic order in methyl alcohol runs between about two and three. It thus appears that, in the range of perchlorate concentration over which the square-root relation holds, the catalysed reaction is less sensitive to methyl alcohol concentration than is the uncatalysed reaction. We think that this difference is of significance in connexion with the mechanism of catalysis by tetra-*n*-butylammonium perchlorate, a subject which will be discussed in Part LVIII.

(7) *Kinetic Effect of Nitromethane and Nitrobenzene.*—Since tetra-*n*-butylammonium perchlorate ion-pairs, which have a dipole moment of 14 D in benzene,<sup>11</sup> exert no noticeable catalytic effect at concentrations somewhat above  $10^{-3}M$ , it is not to be expected that polar aprotic molecules, such as nitro-compounds, which have much smaller moments, and no special situation of charge distribution, such as is present in hydroxy-compounds, will exert appreciable effects except at concentrations above  $10^{-2}$ . Actually the kinetic effects of nitromethane and nitrobenzene become marked only at concentrations of  $10^{-1}M$  upward. Some figures are given in Table 11.

TABLE 11. *Effects of nitro-compounds on the initial specific rates ( $k_1$  in  $sec^{-1}$ ) of reactions of triphenylmethyl chloride (0.1M) with methyl alcohol (0.1M) in benzene at 25°.*

Run	[MeNO <sub>2</sub> ]	10 <sup>5</sup> $k_1$	Run	[PhNO <sub>2</sub> ]	10 <sup>5</sup> $k_1$
Section 4	—	5.6	Section 4	—	5.6
76, 79, 81	0.10	7.5	82 d	0.10	7.3
78, 80 d	0.30	9.6	83 d	0.30	9.3
77	0.50	16.5	90 d	0.68	20
93 d	0.92	35	85 d	0.97	27
95 d	1.85	65	91 d	1.46	44

If we plot these rates against the concentration of the nitro-compounds we find that they lie on steepening curves. The catalysed reaction therefore has no definite kinetic order with respect to nitro-compound. The most conservative estimate that we can make of the range of variation of the formal "order" is that obtained by assuming, as is done in Table 11, that the nitro-compounds are basic enough to annul catalysis by the relatively trifling amount of adventitious hydrogen chloride, and that, accordingly, the catalysed rate is to be taken as the excess over the hydrogen-chloride-free rate, as evaluated in Section 4. If now we plot the logarithm of this excess rate against the logarithm of the concentration of nitro-compound, we get similar curved graphs, each indicating a formal kinetic order running from well below 1.0 to about 1.5 or somewhat above, over the range of the

<sup>11</sup> Luder, Kraus, Kraus, and Fuoss, *J. Amer. Chem. Soc.*, 1936, **58**, 225.

data. The change in formal order would be greater if the nitro-compounds were not basic enough to behave as suggested.

We conclude that we are dealing, not with a specific "push" or "pull" of some precisely placed nitro-molecule, but with a co-solvent effect, which depends on penetrating Coulombic forces, and could not be described otherwise than in statistical terms.

(8) *Kinetic Effect of Phenol.*—This accelerating effect is strong at concentrations of phenol from  $10^{-2}M$  upward. Some illustrative results are in Table 12. We take the

TABLE 12. Effect of phenol on the initial specific rate ( $k_1$  in  $\text{sec.}^{-1}$ ) of reaction of triphenylmethyl chloride (0.1M) in methyl alcohol (0.05M) in benzene at  $25^\circ$ .

Run	[PhOH]	$10^5 k_1$	Run	[PhOH]	$10^5 k_1$
252, 291, 359	—	2.6	406	0.0427	41.3
404	0.0107	11.7	408	0.0640	62.5
405	0.0213	21.5	409	0.0980	108

phenol-free rate as its actual experimental value, including the small catalysis by adventitious hydrogen chloride, because methyl alcohol does not annul this, and therefore it can be taken as certain that phenol will not do so.

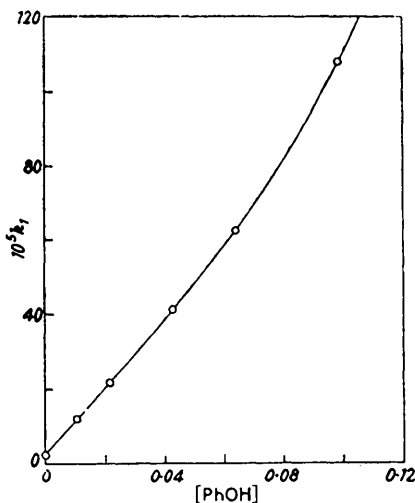


FIG. 8. Effect of phenol on the initial specific rate of reaction of triphenylmethyl chloride (0.1M) with methyl alcohol (0.05M) in benzene at  $25^\circ$ .

This catalysis was investigated by Swain,<sup>1</sup> who reported that the reaction was of "first order in trityl chloride, first order in methanol . . . also first order in phenol, hence again exactly third order overall." However, Swain records the use in this reaction of only two concentrations of phenol; and had we confined our observations to so few concentrations, or to such a narrow range, we also might have thought (very tentatively) that the reaction was in principle of first order in phenol. Actually the tabulated observations, covering a 9-fold concentration range, as well as other series which we could cite, lie on a nearly straight, but actually slowly steepening, curve, as shown in Fig. 8. As will appear in the next paper, when we change the reaction from methyl-alcoholysis to benzyl-alcoholysis, the rate curve, corresponding to that in Fig. 8, steepens more sharply, retaining its curvature, indicative of an inconstant, fractional, kinetic order, greater than unity, down to as low concentrations and catalytic effects as can be measured with accuracy.

(9) *Modifications produced in the Kinetic Effect of Tetra-*n*-butylammonium Perchlorate by Other Added Substances, especially Tetra-*n*-butylammonium Chloride.*—The strong accelerating effect of tetra-*n*-butylammonium perchlorate on the methyl-alcoholysis of triphenylmethyl chloride in benzene is very easily quenched by various added substances. Tetra-*n*-butylammonium chloride, which retards reaction in the absence of the perchlorate, quenches the perchlorate catalysis much more strongly: chloride equivalent to a few units

per cent. of the perchlorate is sufficient to destroy most of the catalytic effect of the latter. Other saline chlorides, such as tetraethylammonium chloride and tri-*n*-butylammonium chloride, act in a qualitatively similar way. Tetra-*n*-butylammonium iodide accelerates the methyl-alcoholysis in the absence of the perchlorate, but it still suppresses the catalytic effect of the perchlorate, in much the same qualitative way as any of the saline chlorides. The tertiary bases, pyridine and tri-*n*-butylamine, also suppress the catalysis of perchlorate. All these effects are illustrated in Table 13.

TABLE 13. *Effect of added substances (X) on the initial specific rate ( $k_1$  in sec.<sup>-1</sup>) of reaction of triphenylmethyl chloride (0.1M) with methyl alcohol (0.1M) under catalysis by tetra-*n*-butylammonium perchlorate (P) in benzene at 25°.*

Run	10 <sup>3</sup> [P]	10 <sup>3</sup> [X]	10 <sup>3</sup> <i>k</i> <sub>1</sub>	Run	10 <sup>3</sup> [P]	10 <sup>3</sup> [X]	10 <sup>3</sup> <i>k</i> <sub>1</sub>	Run	10 <sup>3</sup> [P]	10 <sup>3</sup> [X]	10 <sup>3</sup> <i>k</i> <sub>1</sub>
X = Tetra- <i>n</i> -butylammonium chloride.			X = Tetraethylammonium chloride.			X = Tetra- <i>n</i> -butylammonium iodide.					
318	1.86	—	42.7	216	0.10	—	20.2	182 c, 306	0.20	—	23.0
328	"	0.0039	33.3	256	"	0.0061	17.8	—	"	0.020	9.0
326	"	0.0065	29.2	269	"	"	17.4	—	"	1.00	8.0
329	"	0.0078	27.5	261	"	0.039	6.9	216	0.10	—	20.2
325	"	0.013	22.5	257	"	0.10	6.5	283	"	0.010	11.0
323	"	0.026	16.5					282	"	0.100	9.3
327	"	0.065	10.3	X = Tri- <i>n</i> -butylammonium chloride.				X = Pyridine.			
322	"	0.13	8.3	216	0.10	—	20.2	305	2.00	—	43.3
320	"	0.65	6.2	267	"	0.0029	19.5	37	"	100.0	5.0
216	0.10	—	20.2	264	"	0.0058	14.0	X = Tri- <i>n</i> -butylamine.			
225	"	0.0028	8.4	263	"	0.012	10.8	216	0.10	—	20.2
231	"	0.0057	6.7	215	"	0.029	9.5	281	"	0.011	14.3
								280	"	0.11	8.8

There is no doubt that, among these added substances, tetra-*n*-butylammonium iodide and the two tertiary amines themselves displace chlorine from triphenylmethyl chloride. Until the kinetics of these displacements, as well as the kinetics of the subsequent changes undergone by their products in the presence of methyl alcohol, and, in particular, the kinetic effects of tetra-*n*-butylammonium perchlorate on all these processes, have been separately studied, it would be absurd to try to analyse the overall effects here under observation; and we have not attempted it. The one case, in which we could reasonably hope to solve the problem of the kinetic functional form of the quenching, is that of quenching by saline chlorides; and the simplest chloride to consider in association with tetra-*n*-butylammonium perchlorate is obviously tetra-*n*-butylammonium chloride, since, by the use of identical cations, we avoid uncertainties of cation exchange between the saline ion-pairs. For this case, the series of runs nos. 318—329, at the head of Table 12, provide suitable numerical material.

When these data are plotted, they show a rate curve, which, as the concentration of saline chloride is increased, falls towards an asymptote at or near to the uncatalysed specific rate, determined in Section 4 as  $5.6 \times 10^{-5}$  sec.<sup>-1</sup>. The amounts of saline chloride required to produce this fall of rate lie in the range  $10^{-6}$ — $10^{-3}$ M; and, as the amount present when the uncatalysed rate is nearly reached is still less than  $10^{-3}$ M, and so is too little to produce that suppression of the uncatalysed rate which is discussed in Section 5, we can evidently treat the uncatalysed and the perchlorate-catalysed rates as additive, and take the former rate term as a constant over the range of salt concentrations considered. Thus the perchlorate-catalysed rate is simply the excess of the observed rate over  $5.6 \times 10^{-5}$  sec.<sup>-1</sup>, throughout the concentration range.

Now there are two broad ways in which a saline chloride could be imagined to reduce the perchlorate-catalysed rate. The perchlorate itself obviously intervenes in a step which is rate-influencing for the catalysed reaction: the saline chloride might interfere with that, by withdrawing perchlorate ion. Alternatively, if the reaction has a product-controlling step, in which potential substituting agents compete for a slowly produced



intermediate, the saline chloride might intervene there, and so determine a reversion to triphenylmethyl chloride. Had we not had for reference our conductance results for mixed salts (Part LIII), we should have considered the first of these possibilities very seriously: the ion-pair chloride might conceivably have withdrawn perchlorate ions to give stable, but catalytically ineffective, mixed triple anions. However, the conductance studies show that that cannot be the cause, not even a contributing cause of any importance, of the very sensitive counter-catalytic effect here under discussion: our triple-ion stability constants show that, if perchlorate ion is not withdrawn by a relatively large amount of perchlorate ion-pair, it will not be withdrawn by a much smaller amount of chloride ion-pair.

Therefore we turn to the second possibility, which is that the saline chloride enters into competition for an intermediate in limited supply. So far as concerns the determination of the eventual product, such a competition must be with methyl alcohol; but so far as concerns the catalysed rate, the competition is not necessarily with methyl alcohol

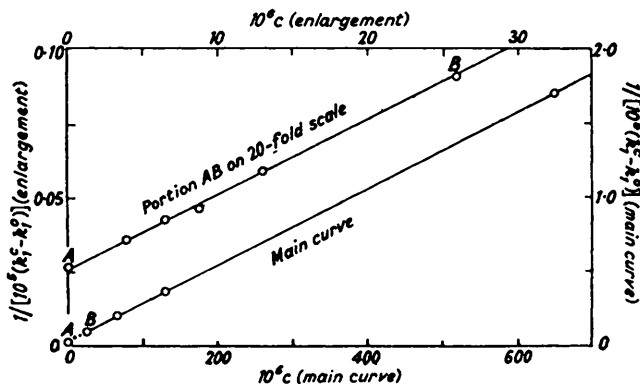


FIG. 9. Suppression by tetra-*n*-butylammonium chloride of catalysis by tetra-*n*-butylammonium perchlorate (0.0018*M*) of the reaction of triphenylmethyl chloride (0.1*M*) with methyl alcohol (0.1*M*) in benzene at 25°.

Plot of the reciprocal of the catalysed part of the specific rate against the concentration of the rate-suppressing agent. The initial part of the main curve contains more points than can be entered clearly, and is therefore shown separately on an enlarged scale.

alone, since the perchlorate ion itself may co-operate with one of the competitors. Other variants of this general type of mechanism can arise, according to whether the chloride enters the competition as a simple chloride ion, or as an ion-pair, or as a triple anion, and so on. This latter group of variants can be distinguished by the data for runs 318—329, in which, although the concentrations of perchlorate and methyl alcohol were kept constant, the concentration of the saline chloride was varied over a 167-fold range. The variant which best fits the data is that the saline chloride competes as its ion-pair.

The mass-law equation for rate in these circumstances is

$$k_1^{pc} - k_1^{p0} = \frac{k_1^{p0} - k_1^{00}}{1 + \rho c}$$

where  $k_1^{pc}$  is the specific rate in the presence of the saline perchlorate in concentration  $p$ , and the saline chloride in concentration  $c$ , whilst  $\rho$  expresses by what factor the specific rate of capture of the intermediate by the saline chloride ion-pair is greater than the rate (not specific rate) of its capture by the other competitors. This equation assumes that practically the whole of the saline chloride is present as ion-pairs; and certainly, at the salt concentrations here employed, this condition is well fulfilled, so that we should expect a satisfactory numerical agreement.

For the series of runs 318—329,  $k_1^{p0} = 42.7 \times 10^{-5} \text{ sec.}^{-1}$ ; as shown in Section 4,  $k_1^{00}$  is  $5.6 \times 10^{-5} \text{ sec.}^{-1}$ . The dependent variable in the above equation is  $k_1^{pc}$ , and the independent variable is  $c$ . The test for intervention of the saline chloride by competition, the actual competitor being the ion-pair, is thus to plot  $1/(k_1^{pc} - k_1^{p0})$  against  $c$ : this should give a straight line of slope  $\rho$ . As will be seen from Fig. 9, this law is very well obeyed. The slope of the line gives  $\rho = 95500 \text{ l. mol.}^{-1}$ .

There is thus a competition for a slowly formed intermediate, and one of the

competitors, that which causes reversion to triphenylmethyl chloride, is tetra-*n*-butylammonium chloride, very probably in ion-pair form. Its opponent in the competition, that which leads to the alcoholysis products, must contain methyl alcohol, and it seems qualitatively obvious that it must also involve the perchlorate, though we have not proved this formally. This appears to follow, partly from the large value of  $\rho$ , which suggests that some essential part of the opponent must be in low concentration; and partly from the fact that the last few figures in the first section of Table 13, although they are not suitable for quantitative treatment, do indicate that, with a smaller concentration of perchlorate,  $\rho$  takes on a still larger value.

It will not be overlooked that two conclusions have been drawn about perchlorate which obviously present a problem in reconciliation. The salt is a catalyst: therefore it must be intervening *in* a rate-controlling process, since it is providing a by-pass to a process which would be rate-controlling in its absence. But, when a second substituting agent is provided, the salt also appears to be involved in a product-controlling competition for some slowly supplied intermediate: therefore it must be intervening *after* the completion of an earlier slow step. This dilemma cannot be resolved on the internal evidence of this paper; but we shall set it beside the special problems presented by the kinetic investigations of the accompanying papers, and attempt to resolve them all in Part LVIII.

#### EXPERIMENTAL

*Materials.*—Their preparation and purification is described in Part LIV.

*Methods.*—Calculated volumes of benzene solutions of all the materials to be used in a run were measured at 25°, and mixed in a 50 ml. flask, the triphenylmethyl chloride solution being introduced last. A 5 ml. sample was at once withdrawn, and run into 30 ml. of acetone at -80°: it was then titrated with a solution of triethylamine in benzene to a bromophenol blue indicator. Other samples, withdrawn after various intervals, were treated similarly. Various concentrations of standard triethylamine were used, ranging from 0.001M to 0.05M.

*Results.*—The essential results have already been summarised. The details given in Table 14 of illustrative runs are intended to show the commonly observed rise of specific rate, owing to autocatalysis by hydrogen chloride, succeeded, if the run is followed far enough, by a fall,

TABLE 14. *Illustrations of the kinetic course of the reaction of triphenylmethyl chloride with methyl alcohol in benzene at 25°.*

Run 130: Initially, [Ph <sub>3</sub> CCl] = 0.1M, [MeOH] = 0.1M.			Run 132: Initially, [Ph <sub>3</sub> CCl] = 0.1M, [MeOH] = 0.01M.			Run 149: Initially, [Ph <sub>3</sub> CCl] = 0.1M, [MeOH] = 0.1M, [ <i>n</i> -Bu <sub>4</sub> NCl] = 0.0396M.		
<i>t</i>	% Reac.	10 <sup>3</sup> <i>k</i> <sub>1</sub>	<i>t</i>	% Reac.	10 <sup>3</sup> <i>k</i> <sub>1</sub>	<i>t</i>	% Reac.	10 <sup>3</sup> <i>k</i> <sub>1</sub>
0	0.39	—	0	2.04	—	0	0.297	—
0.5	0.60	7.0	0.5	2.18	0.46	0.5	0.350	1.77
1	0.85	7.6	1	2.32	0.42	1	0.410	1.92
2	1.45	9.0	2	2.54	0.40	2	0.520	1.87
3	2.00	9.8	5	3.32	0.42	5	0.885	1.98
5	3.30	10.3	10	4.40	0.39	10	1.51	2.18
10	7.20	11.8	15	5.44	0.38	15	2.13	2.25
15	10.5	11.8	30	9.50	0.41	40	5.30	2.15
30	11.0	6.2						

owing to reversibility. The autocatalytic rise may be reduced or may disappear, if the methyl alcohol is so reduced that only small concentrations of hydrogen chloride are formed in the measured part of the run; and again, it is reduced if tetra-*n*-butylammonium chloride is present in quantity comparable to the hydrogen chloride formed in the measured reaction. Constants  $k_1$  are calculated from the usual first-order kinetic equation,  $k_1 = (1/t) \ln\{a/(a-x)\}$

We thank the British Council for a Travelling Fellowship (to F. S. M.).

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,  
UNIVERSITY COLLEGE, GOWER ST., LONDON, W.C.1.

[Received, October 5th, 1956.]