239. *Mechanism of Substitution at a Saturated Carbon Atom. Part LVII.* Kinetics of the Reaction of Triphenylmethyl Chloride with Benzyl Alcohol in Benzene.*

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The work of Hawthorne and Cram on the benzyl-alcoholysis of triphenylmethyl chloride in benzene has been revised. It has been found that the reaction is of first order in triphenylmethyl chloride, and that, contrary to the previous authors' conclusions, it is of no particular order in benzyl alcohol, and neither is it, when phenol is present, of any particular order in phenol. In the rate-controlling stage of the alcoholysis, these hydroxy-compounds, even the alcohol which will eventually react, appear to function kinetically only as polar co-solvents, as also do polar substances which could not react, such as nitromethane and nitrobenzene.

Hydrogen chloride catalyses the alcoholysis. Tetra-*n*-butylammonium chloride retards it, first, by suppressing any catalysis or autocatalysis due to hydrogen chloride and, secondly, by a retarding mechanism of its own. Tetra-*n*-butylammonium perchlorate strongly accelerates the alcoholysis, and the corresponding nitrate produces a much milder acceleration. The catalytic effect of the perchlorate is suppressed by added nitrate, and is suppressed much more strongly by tetra-*n*-butylammonium chloride.

From these results, and in the light of the preceding paper, it is concluded that the alcoholysis is a reaction of S_N1 type, starting with a slow and rate-controlling step, in which the alcohol does not yet undergo any change, and continuing with a fast and product-controlling reaction between the carbonium ion, which is the product of the first step, and the alcohol. A saline chloride depresses the uncatalysed rate by competitively intervening in the product-controlling step. A saline chloride destroys catalysis by hydrogen chloride by combining with the catalyst. It suppresses catalysis by a saline perchlorate by competing for a slowly produced intermediate. The kinetic effects of tetra-*n*-butylammonium nitrate are probably complicated by reversible conversion of the triphenylmethyl chloride into triphenylmethyl nitrate.

The " push-pull " mechanism of Swain has no place in this picture, and is, indeed, excluded by the results.

SWAIN claimed that nucleophilic substitutions, not only of triphenylmethyl chloride in benzene, but of alkyl halides generally in various solvents, present a " unity of mechanism," and necessarily involve " push-pull termolecular " processes; and further that, in benzene, in which the full molecularity can be reflected in kinetic order, " the result is always a push-pull termolecular mechanism with exactly third order kinetics." [1]

Hawthorne and Cram took these ideas as the starting point of an investigation of the reactions of triphenylmethyl chloride with benzyl alcohol, and with several substituted benzyl alcohols, without and with added phenol, in solvent benzene.[2] As this work constitutes the main piece of explicit collateral support for Swain's thesis we have examined its experimental foundations.

Actually, Hawthorne and Cram noticed some kinetic discrepancies. But they left them either poorly explained or unexplained; and they never seem to have been led by them to question the basic validity of Swain's work on which they are attempting to build.

Thus the supposed unity of mechanism was not reflected in their experiments in a

* Part LVI, preceding paper.

[1] Swain *et al.*, *J. Amer. Chem. Soc.*, (*a*) 1948, **70**, 1119; (*b*) p. 2794; (*c*) 1950, **72**, 2794; (*d*) 1951, **73**, 2813; (*e*) 1953, **75**, 136; (*f*) 1955, **77**, 1122; (*g*) p. 3727; (*h*) p. 3731; (*i*) p. 4681.
[2] Hawthorne and Cram, *ibid.*, 1954, **76**, 3451.

unity of kinetic form. Whilst a number of their reactions appeared to fit the third-order rate-law, some, *e.g.*, those with 4-chloro- and 4-nitro-benzyl alcohol in the presence of phenol, required a mixed-order equation,

$$-d[RCl]/dt = k_2[RCl][R'OH] + k_3[RCl][R'OH]^2$$

and a number, *e.g.*, those with benzyl alcohol, and with 4-methyl- and 4-methoxy-benzyl alcohol, in the presence of phenol, fitted the simple second-order equation. As to these last cases, Hawthorne and Cram comment that " the additional third order term was doubtless present, but its effect was always within the experimental error." Now this is an unacceptably poor explanation. For the paper contains an independent way of arriving at these particular k_3 values, and if the experimental error were really large enough to absorb them then it would be at least of the same order of magnitude as *all* the k_3 values quoted (even though they are quoted to three significant figures). This makes nonsense of kinetic support for the termolecular mechanism.

The other main example requires reference to the fact that, just as Swain ran his reactions between triphenylmethyl chloride and hydroxy-compounds in the presence of pyridine (" to take up the hydrogen halide formed " [1a]), so Hawthorne and Cram conducted theirs in the presence of triethylamine. In these conditions, the reaction with phenol was one of those which was said to give agreement with the second-order rate-law. Its absolute rate in the presence of triethylamine was much greater than in the presence of pyridine. These results led the authors to conclude (*a*) that the phenol and triethylamine are practically completely combined to form the triethylammonium phenoxide ion-pair, and (*b*) that the transition state of the measured reaction consists of one molecule of triphenylmethyl chloride and one molecule of triethylammonium phenoxide as ion-pair. They then asked where was the " kinetically invisible " third molecule demanded by the mechanism, not only in this case, but also in the other cases in which the kinetics seemed to conform partly or wholly to a second-order rate-law. They admitted that they could not find a satisfactory answer to that question.

(1) *The Experimental Conditions.*—Hawthorne and Cram examined their reactions of triphenylmethyl chloride with hydroxy-compounds in benzene solutions, which contained triethylamine equivalent to the alkyl halide and were saturated with, and carried in suspension, triethylamine hydrochloride, added initially in solid form in excess, and also precipitated in the course of the reaction. This is a recipe for profound kinetic complications.

In the reaction with phenol they could compare their rate in the presence of triethylamine and its hydrochloride with that obtained by Swain in the presence of pyridine and pyridine hydrochloride. Though there was a large difference, they seem not to have considered the likelihood that almost any moderately basic amine, as a strong nucleophile, must distort the kinetics of reactions of triphenylmethyl chloride with generally less nucleophilic hydroxy-compounds. They do mention that, on working up products, they did not isolate any quaternary ammonium salt. That alone could mean, either that it is formed too slowly, or that it is formed reversibly and rapidly. One may suppose that, ignoring general questions of nucleophilic power, they were excluding the latter interpretation, on account of Swain's statement [1a] that " the reaction between trityl chloride and tertiary amines is negligibly slow." •

We have shown that, as one ought to expect, this statement is not correct (Part LIV), and that, in particular, triphenylmethyl chloride reacts with pyridine and with tri-*n*-butylamine at rates comparable to that of its exchange of chlorine with a saline chloride, and therefore considerably faster than the rates of its reaction with, for example, benzyl alcohol. That no quaternary salt was isolated is irrelevant, because the salt itself

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• In the case of triphenylmethyl bromide, Swain and Eddy offer a numerical measure of the slowness, stating that it reacts with pyridine 10^6 times more slowly than with methyl alcohol.[1b]. But they present no account of the experiments on which they base this statement.

could react with benzyl alcohol, though not at the same rate as the chloride, to which it would concurrently revert.

In Hawthorne and Cram's conditions there are a number of partly compensating disturbances. The net effect of the amine is to reduce the rate of reaction with the alcohol. In principle, the dissolved amine hydrochloride will reduce it further, but this effect is unimportant. However, the suspended salt, 1 g. per 100 c.c. in their conditions, super-poses an appreciable surface reaction on the homogeneous one, thus producing a rate increase in the measured overall reaction. The existence of the heterogeneous component implies that any integral reaction order apparently followed by the overall reaction is accidental. All this applies to the otherwise uncatalysed reaction with the alcohol. If we are studying the nucleophilic catalysis of the reaction, as by tetra-*n*-butylammonium perchlorate, then the addition of other nucleophiles, such as tertiary amines and saline chlorides, produces more drastic retarding effects. It is not necessary to record all the details of our survey of this complex situation, because its conclusion is simply that the method must be abandoned. However, the selection of figures in Table 1 will give an idea of the magnitude of the kinetic effects involved.

TABLE 1. *Initial specific rates* $(k_1$ *in sec.*$^{-1})$ *of disappearance of triphenylmethyl chloride by reaction with benzyl alcohol in benzene at 30° in the presence of various added substances.*

(Initially, $[CPh_3Cl] = [C_7H_7 \cdot OH] = 0.05M$, throughout.)

Run no.	$[Bu^n{}_4NClO_4]$	$[Et_3N]$	$[Bu^n{}_3N]$	Suspended Et_3N,HCl	10^5k_1
Cf. Table 2	—	—	—	—	0.93
44, 67	—	0.05	—	—	0.50
71, 72	—	0.05	—	1 g./100 c.c.	0.55
110, 128, 182	0.002	—	—	—	23.8
196	,,	—	0.000005	—	16.7
195	,,	—	0.00005	—	2.8
193	,,	—	0.0005	—	2.1

The figures there represent initial specific rates of destruction of triphenylmethyl chloride, $-d[RCl]/[RCl]dt$, as followed by the rate of appearance of acid, or the rate of neutralisation by the acid of initially added base, and derived from the smoothed curve of the early kinetic readings. The basic rate, *i.e.*, with nothing added except the reagents, is really a little too high as given, because of catalysis by adventitious hydrogen chloride, which was present in the experiment cited to the concentration $3 \times 10^{-5}M$ (cf. the preceding paper, Section 4). However, this does not change the picture, or alter the conclusion that the experimental conditions require to be simplified.

The simplification we have adopted is, of course, to omit the tertiary amine and the amine hydrochloride, and to study initial rates, as illustrated in Table 1. The reaction is reversible, with an equilibrium constant,

$$K = [CPh_3 \cdot O \cdot CH_2Ph][HCl]/[CPh_3Cl][CH_2Ph \cdot OH] = 0.0065$$

at 30°. But the initial rate of the forward reaction remains steady for long enough to allow it to be determined, before the rate begins to fall on account of reversibility. Domin-ating autocatalysis, due to developed hydrogen chloride, was not clearly observed, though there can be no doubt that autocatalysis was present and tended to delay the onset of the ultimately dominating retardation due to reversibility. When the reagents were present in equivalence, the forward reaction proceeded to 7.3% of the stoicheiometric maximum; and, naturally, with either reagent in excess, the other was consumed more extensively. For the uncatalysed, or mildly catalysed, reaction, it was easily possible to obtain kinetic points at tenth-per-cent. intervals or less over the first 1—2% of the stoicheiometric reaction, or, say, the first 5—20% of the realisable reaction, and this was adequate for good initial rates. For the faster catalysed reactions, our initial rates are less reliable. The main source of error involved in our method is that of catalysis by adventitious

hydrogen chloride; but it was not a large error, and ways of coping with it were worked out in some detail as described in the preceding paper.

(2) *Dependence of Rate on the Concentrations of Reactants.*—Our experiments have shown that the benzyl-alcoholysis of triphenylmethyl chloride in benzene is of first order in triphenylmethyl chloride, but has no simple and exact order with respect to benzyl alcohol.

These points, particularly the second, are illustrated in the comparable rate figures given in Table 2. If we plot the logarithm of the specific rate with respect to triphenyl-methyl chloride against the logarithm of the concentration of benzyl alcohol, over the investigated 25-fold range of benzyl alcohol concentration, we obtain a continuously steepening curve, with a slope rising from about 1 to 2·5 as the concentration increases, and with no sign of an arrest of slope at 2 or at any other intermediate value.

TABLE 2. *Effect of concentrations of reactants on the initial specific rate (k_1 in sec.$^{-1}$) of disappearance of triphenylmethyl chloride by reaction with benzyl alcohol in benzene at 30°.*

Run	$[CPh_3Cl]$	$[C_7H_7 \cdot OH]$	$10^5 k_1$	% HCl at equilib.*	Equil. const. K
203	0·05	0·020	0·37	4·8	0·0067
211	,,	0·0325	0·63	6·0	0·0065
212	,,	0·040	0·83	6·7	0·0066
69, 102, 116 } 133, 163 }	,,	0·050	0·93	7·3	0·0062
94	0·15	,,	0·93	12·6	0·0063
213	0·05	0·060	1·67	7·6	0·0056
201, 202 } 206, 207 }	,,	0·100	2·77	11·0	0·0072
62, 63, 64 } 142, 143 }	,,	0·150	5·7	12·9	0·0067
74	,,	0·500	67	25·5	(0·0090)
					————
					0·0065

* Calculated taking 0·05M = 100%.

This result for benzyl-alcoholysis is the same as that obtained for methyl-alcoholysis, except that the formal order for methyl-alcoholysis rose just a little more steeply, from about 1 to 3 (instead of to 2·5) in the concentration range over which benzyl-alcoholysis has been investigated; and for methyl alcoholysis the relation was followed to orders below 1 by a downward extension of the concentration range (cf. Fig. 1 of preceding paper). The conclusion is clearly the same : neither two, nor any other small and necessary number of molecules of the alcohol, have exclusive functions and defined positions in the transition state of the rate-controlling step of the measured reaction : there is no " push-pull " by alcohol molecules. This being so, the rest of the argument of Hawthorne and Cram's paper, as of all Swain's papers on this subject, falls to the ground.

This applies, *inter alia*, to a paper by Swain, Moseley, and Bown, to which we have not previously referred.[1h] In it, the push-pull theory was developed on supposedly quantitative lines, which Hawthorne and Cram attempt to apply. In this theory the nucleophile N and electrophile E in the transition state

$$N \cdots \cdots R\!-\!Cl \cdots \cdots E$$
$$(n) \qquad (s) \ (s') \qquad (e)$$
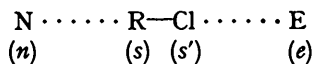
are assigned factors n and e of pushing and pulling strength, respectively, and the alkyl halide factors s and s' of sensitivity to the pushing and pulling. The law of combination of the factors is assumed to be

$$\log (k/k°) = ns + es'$$

where $k°$ refers to rate with a standard N and E. Obviously, if either or both of the molecules assigned as N and E have not these exclusive functions, *i.e.*, if there is in fact no " push-pull," the considerable numerical elaboration offered in the paper of Swain, Moseley, and Bown cannot have its supposed significance.

The formal order of benzyl-alcoholysis with respect to benzyl alcohol, and the absolute

rate of the reaction, are both still falling as the concentration of benzyl alcohol is reduced, down to the lowest concentration investigated (0·02M). We cannot be sure that the formal order in alcohol would fall to zero at still lower alcohol concentrations, as appears to happen in methyl-alcoholysis; but it is certainly tending in that direction. Furthermore, as the concentration of alcohol is diminished, and the medium is becoming more like pure benzene, the rate is not only becoming less dependent on the alcohol, but is also falling, and is evidently tending to a value well below the lowest recorded in Table 2, *viz.*, 0·37 × 10⁻⁵ sec.⁻¹. It is of interest to observe that this lowest recorded rate is already lower than the rate of chloride exchange in benzene, *viz.*, 0·503 × 10⁻⁵ sec.⁻¹ at 30°. This makes it clear that these two substitutions of triphenylmethyl chloride, despite that each alone has the kinetic features of an S_N1-type mechanism, are not fully rate-determined by a completely identical process.

Table 2 contains some measurements of the equilibrium composition, as approached from the side of triphenylmethyl chloride and benzyl alcohol. We have done some experiments on equilibrium composition, as approached from the side of benzyl triphenylmethyl ether and hydrogen chloride, and get nearly the same figures, actually very slightly lower ones, when expressed as percentages of hydrogen chloride, probably because of the difficulty of working with all but highly dilute solutions of hydrogen chloride in benzene, from which solvent it escapes somewhat easily.

(3) *Kinetic Effect of Hydrogen Chloride.*—The effects of added substances on the rate of the benzyl-alcoholysis have been investigated less fully than were the corresponding effects on methyl-alcoholysis (see preceding paper), but sufficiently to show that the pattern of kinetic phenomena is generally similar.

The catalytic effect of hydrogen chloride is illustrated in Table 3, which shows that hydrogen chloride increases the rate of the benzyl-alcoholysis, but restricts the extent to which this reaction can proceed. The figures indicate that the measurable kinetic effect is linear, just as for methyl-alcoholysis.

TABLE 3. *Effect of hydrogen chloride on the initial specific rate (k_1 in sec.⁻¹) of benzyl-alcoholysis of triphenyl chloride in benzene at 30°.*

(Initially, [CPh₃Cl] = [C₇H₇·OH] = 0·05M, throughout.)

Run No.	10³[HCl]	10⁵k_1	HCl (%) at equil.	Ether (%) at equil.*
403	0·03	0·88	7·3	7·3
405	0·90	2·3	7·6	5·8
404	3·50	6·7	10·0	2·9

* Calc. on the basis 0·05M = 100%.

(4) *Kinetic Effect of Tetra-n-butylammonium Chloride.*—Just as for methyl-alcoholysis, so for benzyl-alcoholysis, two phases can be distinguished in the kinetic effect of the progressively added salt. First, very small amounts of the salt will effect a limited depression of the rate, *e.g.*, by 15%. Then, nothing more happens to the rate while the

TABLE 4. *Effect of tetra-n-butylammonium chloride on the initial specific rate (k_1 in sec.⁻¹) of benzyl-alcoholysis of triphenylmethyl chloride in benzene at 30°.*

(Initially, CPh₃Cl = 0·05M, and C₇H₇·OH = 0·15M, throughout.)

Run	[Buⁿ₄NCl]	10⁵k_1	Run	[Buⁿ₄NCl]	10⁵k_1
Table 2	—	5·7	141, 149	0·02	4·7
153	0·0002	4·8	160	0·04	3·3
146, 159	0·001	4·8	144, 148	0·06	1·9

concentration of salt is further increased by 10 times or even 100 times. But when the concentration of salt begins to approach comparability with the concentration of benzyl alcohol, then a new, and strong, rate-depression sets in. These relations are illustrated in Table 4.

Our interpretation is that the first rate-depression, represented in Table 4 by the reduction of $10^5 k_1$ from 5·7 to 4·8, arises from the destruction by the added chloride ion of catalysis by the adventitious hydrogen chloride. The chemistry of this is as described in the preceding paper (Section 4). The second rate-depression, that which in Table 4 carries $10^5 k_1$ from 4·8 down to 1·9 is explained as a common-ion effect in a mechanism of S_N1 type, *i.e.*, an effect of a competition between the saline chloride and benzyl alcohol, for the intermediate formed in an earlier slow step from the triphenylmethyl chloride (cf. preceding paper, Section 5).

In the presence of tetra-*n*-butylammonium chloride, the benzyl-alcoholysis proceeds to an equilibrium, which is strongly displaced in the direction favouring benzyl triphenyl-methyl ether and hydrogen chloride. For example, with 0·04M of the salt, ether formation proceeded to more than 50% of the stoicheiometric maximum. This happens because the salt combines with hydrogen chloride to give the corresponding hydrogen-dichloride.

(5) *Kinetic Effect of Tetra-*n-*butylammonium Perchlorate and Nitrate.*—The former salt accelerates the benzyl-alcoholysis strongly; and the latter accelerates it more mildly. This is illustrated in Table 5. We believe that the former effect is the simpler, and that the latter is the net result of partly compensating effects, including the conversion of tri-phenylmethyl chloride into the corresponding nitrate, with subsequent benzyl-alcoholysis under the retarding influence of the saline nitrate, which is now a common-ion salt.

TABLE 5. *Effect of tetra-*n-*butylammonium perchlorate and nitrate on the initial specific rate* (k_1 *in* sec.$^{-1}$) *of benzyl-alcoholysis of triphenylmethyl chloride in benzene at* 30°.

(Initially, [CPh$_3$Cl] = 0·05M, throughout.)

Salt = Bu$^n_4$NClO$_4$ [C$_7$H$_7$·OH] = 0·05M throughout			Salt = Bu$^n_4$NNO$_3$				
Run	10^3 [Salt]	$10^5 k_1$	Run	[C$_7$H$_7$·OH]	10^3 Salt	$10^5 k_1$	HCl (%) at equil.*
Table 2	—	0·93	Table 2	0·05	—	0·93	7·2
119, 127, 130	0·002	1·37	171	,,	2	4·2	>10
114, 118, 129	0·02	4·4	172	,,	10	13·3	25
112, 120	0·2	12·0	173	,,	20	16·6	37
111	1	16·7	Table 2	0·15	,,	5·7	12·9
110, 128, 182	2	23	179	,,	1	8·3	15
109	4	26	180	,,	10	28	31

* Calc. on the basis 0·05M = 100%.

If we plot the logarithm of the increase, produced by the tetra-*n*-butylammonium perchlorate, in the rate of alcoholysis by 0·05M-benzyl alcohol, against the logarithm of the concentration of the perchlorate, we obtain a curve very similar to that already drawn for the increase produced by the same salt in the rate of alcoholysis by 0·05M-methyl alcohol (cf. Fig. 6 of the preceding paper, p. 1250). The central part of the curve conforms to a slope of $\frac{1}{2}$, but the low-concentration extremity runs lower, whilst at concentrations above 10^{-3}M the slope of the curve falls below $\frac{1}{2}$. We take this to mean that the chemistry of the catalysis of methyl-alcoholysis and benzyl-alcoholysis is similar, and that a fuller investigation of the kinetics of the latter would show the same limiting square-root law, representing the inclusion of just one simple perchlorate ion in the transition state of the rate-controlling process. Kinetic deviations arise, without necessarily upsetting this simple meaning, when the salt is so concentrated that it becomes more aggregated than to ion-pairs, and when the medium and salt conditions render perchloric acid somewhat, but only somewhat, less ionised than the corresponding ammonium salt (cf. preceding paper, Section 6).

The addition of tetra-*n*-butylammonium perchlorate has practically no effect on the composition of the equilibrium to which the benzyl-alcoholysis proceeds. On the other hand, the presence of tetra-*n*-butylammonium nitrate, similarly to that of the chloride, shifts the composition at equilibrium in the direction favouring the ether and hydrogen chloride, as is illustrated in Table 5. All this is consistent with the conclusion, reached

in Part LIII that the anion $(ClHClO_4)^-$ does not exist, but that the anions $(ClHCl)^-$ and $(ClHNO_3)^-$ are both stable in benzene.

(6) *Kinetic Effect of Nitromethane and Nitrobenzene.*—These substances were taken as examples of dipolar but aprotic, non-ionic, molecules. As is to be expected, their addition to the non-polar solvent accelerates the polar reaction we are discussing. These kinetic effects are illustrated in Table 6, which also shows that the nitro-compounds have very little effect on the equilibria to which the reactions proceed.

TABLE 6. *Effects of nitromethane and nitrobenzene on the initial specific rate (k_1 in sec.$^{-1}$) of benzyl-alcoholysis of the triphenylmethyl chloride in benzene at 30°.*

Run	[CPh$_3$Cl]	[C$_7$H$_7$·OH]	[MeNO$_2$]	$10^5 k_1$	HCl (%) at equil.*
Table 2	0·05	0·05	—	0·93	7·3
,,	0·05	0·15	—	5·7	12·9
,,	0·15	0·05	—	0·93	12·6
75—78	0·05	,,	0·37	1·85	7·8
86	,,	,,	0·92	2·7	7·2
89, 104	,,	,,	1·85	6·2	7·2
79	,,	0·15	0·37	11·9	13·1
87	,,	,,	0·92	17	13·2
90, 105	—	—	1·85	30	12·8
			[PhNO$_2$]		
80, 82, 83	0·05	0·05	0·97	2·8	7·3
81, 91, 93	,,	,,	1·95	6·0	7·6
84, 85	,,	0·15	0·97	16·7	13·0
88, 92	,,	,,	1·95	24·0	13·0
95	0·15	0·05	1·95	1·8	13·3

* Calc. on the basis 0·05M = 100%.

The increase of rate due to the added nitro-compounds conform to no constant kinetic order with respect to nitro-compound. The formal order increases with concentration, from well below unity to well above it, in the range investigated. This is a common effect on a polar reaction, of the addition of a polar co-solvent to a non-polar solvent. It indicates stabilisation of the transition state by the polar material, partly locally concentrated, but acting mainly by virtue of the great range of electrostatic forces in the non-polar medium : no precise placing of a fixed small number of polar molecules is involved.

(7) *Kinetic Effect of Phenol.*—Added phenol catalyses the benzyl-alcoholysis. It simultaneously acts as a substituting agent, but only to a very minor extent. Its catalytic effect on the alcoholysis was investigated by Hawthorne and Cram,[2] who, however, used only one concentration of phenol, having apparently accepted, as so certain that it was not worth checking, Swain's generalisation that the alcoholysis would be of third order overall, and of first order in phenol, when phenol was present.

Our results for the dependence of the rate on the concentration of added phenol are shown in Table 7, and in the Figure. From the latter one sees that the kinetic order with
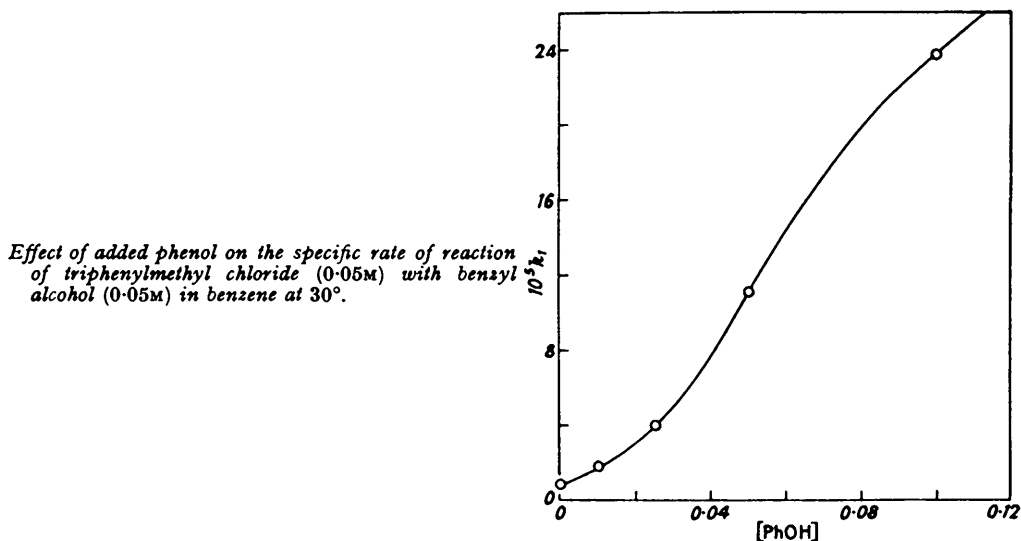
TABLE 7. *Effect of phenol on the initial specific rate (k_1 in sec.$^{-1}$) of benzyl-alcoholysis of triphenylmethyl chloride in benzene at 30°.*

(Initially, [CPh$_3$Cl] = [CH$_2$Ph·OH] = 0·05M, throughout.)

Run	PhOH	$10^5 k_1$	Run	[PhOH]	$10^5 k_1$
Table 2	—	0·93	162, 168	0·050	11·1
165	0·010	1·80	167	0·100	23·8
164	0·025	4·0			

respect to phenol is not unity, and is not even constant. In our concentration range it is between 1 and 2, nearer 2 in the central part of the range, but falling towards 1 at both extremities. This is easily verified by plotting the logarithm of the excess of rate against the logarithm of the phenol concentration, when one obtains a sigmoid curve, with slopes varying between 1 and 2. We therefore suggest that the phenol has the function of a

polar co-solvent. We see in these results no evidence that just one phenol molecule has a precise place and an essential function in the transition state of the rate-controlling step of the alcoholysis.

The equilibrium composition of the reaction mixtures was practically unaffected by the added phenol: all the runs in Table 7 developed 6·6—7·0% of the stoicheiometrically possible amount of hydrogen chloride. The reaction of triphenylmethyl chloride (0·05M) with phenol (0·1M), in the absence of benzyl alcohol, came to equilibrium after about 1% of reaction.

Effect of added phenol on the specific rate of reaction of triphenylmethyl chloride (0·05M) with benzyl alcohol (0·05M) in benzene at 30°.

(8) *Kinetic Effect of Mixtures of Tetra-n-butylammonium Perchlorate, Nitrate, and Chloride.*—The available data are in Table 8. Their most striking feature is the great ease with which a second salt, particularly tetra-n-butylammonium chloride, destroys the positive catalytic effect of tetra-n-butylammonium perchlorate.

TABLE 8. *Effect of mixtures of tetra-n-butylammonium salts on the initial specific rate (k_1 in sec.$^{-1}$) of benzyl-alcoholysis of triphenylmethyl chloride (0·05M) in benzene at 30°.*

Run	[C$_7$H$_7$·OH]	[Bu$^n_4$NClO$_4$]	[Bu$^n_4$NNO$_3$]	[Bu$^n_4$NCl]	10$^5k_1$
Table 2	0·05	—	—	—	0·93
171	,,	—	0·002	—	4·2
110, 128, 182	,,	0·002	—	—	23
183	,,	,,	0·002	—	4·7
197	,,	,,	—	0·00005	5·0
Table 2	0·15	—	—	—	5·7
145, 157	,,	0·001	—	—	93
156	,,	,,	—	0·00002	37
158	,,	,,	—	0·00005	18
155	,,	,,	—	0·0001	11·5
152	,,	,,	—	0·001	4·8
147	,,	,,	—	0·02	4·8

The corresponding phenomenon, as observed for methyl-alcoholysis, is shown in the preceding paper to have the correct functional form for interpretation as an effect of the competitive intervention by the tetra-n-butylammonium chloride as ion-pair in the second and product-forming step of a reaction rate-controlled by a preliminary step in which the substituting agent does not participate. The criterion is that the reciprocal of the excess rate due to the catalysis, or to the partly suppressed catalysis, would be a linear function of the concentration of the suppressing agent. If we apply this test to the set of runs with

0·001M-tetra-*n*-butylammonium perchlorate, and various smaller concentrations of tetra-*n*-butylammonium chloride, remembering that the excess of rate must be reckoned, not from $5·7 \times 10^{-5}$ sec.$^{-1}$, a value which includes some catalysis by adventitious hydrogen chloride, but from $4·8 \times 10^{-5}$ sec.$^{-1}$, the asymptotic rate resulting from suppression of the catalysis (Table 4), the reciprocal of the excess of rate is found to conform to a linear function of the concentration of tetra-*n*-butylammonium chloride to within the experimental error. We may accordingly assume that the same interpretation is applicable. The factor, ρ, representing the ratio of the specific rate of capture of a slowly formed intermediate by the suppressing agent, to the absolute rate of its capture by the reagents which lead by the catalytic route to the alcoholysis product, is given by the slope of the linear plot. It is 107,000 mole^{-1} at the concentrations of benzyl alcohol and tetra-*n*-butylammonium perchlorate used in these experiments.

EXPERIMENTAL

Materials.—These were prepared or purified as described in Part LIV.

Methods.—Stock solutions of the component solutes of the reaction mixtures were prepared in benzene, or, in the case of the more difficultly soluble salts, in solutions of benzyl alcohol in benzene. The reaction mixtures were made up in the thermostat at $30·0° + 0·02°$, the triphenylmethyl chloride being added last, after the attainment of thermal equilibrium. Samples were quenched in cooled dry benzene and were titrated quickly with 0·05 or 0·01M-solutions of triethylamine in benzene, bromophenol-blue being the indicator. Some samples were quenched in a benzene solution of triethylamine and were then titrated with hydrochloric acid. The results by this method were the same.

Results.—The more important initial specific rates have been cited in previous Tables. Initial rates were taken from smoothed curves of readings taken in the initial parts of runs. These curves do not give steady first-order rate constants, $k_1 = -d[RCl]/[RCl]dt$, mainly because reversibility leads to a fall after the reaction has proceeded beyond 5, 10, or 20%, according to circumstances, of its way towards equilibrium. The general character of these downward drifts in k_1 is indicated by the examples in Table 9.

TABLE 9. *Illustrating the calculation of initial specific rates from slowly drifting, integrated, first-order rate constants, obtained from rate curves.*

Run 201.   Equilibrium extent of reaction : 11·0%.

Reaction (%)	0·1	0·2	0·3	0·4	0·5	0·75	1·0	1·5
$10^5 k_1$	2·75	2·77	2·63	2·67	2·61	2·50	2·43	2·28

Run 405.   Equilibrium extent of reaction : 5·8%.

Reaction (%)	0·2	0·4	0·6	0·8	1·0	1·5	2·0	3·0
$10^5 k_1$	2·25	2·25	2·22	2·20	2·17	2·17	2·13	1·92

Run 155.   Equilibrium extent of reaction : *ca.* 13%.

Reaction (%)	1	2	3	4	5	6	7	8
$10^5 k_1$	11·3	11·2	10·7	10·5	10·4	10·4	10·3	10·1

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