TABLE II

RELATIVE REACTION RATES OF ALIPHATIC ALCOHOLS

Alcohol	K^9	K (this work)	K^{10}	K^{11}	% reacted[12]
$(CH_3)_3SiCH_2OH$	.....	2.92	...	..	..
CH_3OH	1.000	1.00	1.00	1.00	55.6
C_2H_5H	0.961	0.82	0.46	0.81	46.9
n-C_3H_7OH	.782	..	.36	.79	46.9
n-C_4H_9OH	.972	..	.40	.80	46.8
n-$C_5H_{11}OH$	.908	..	.43	.98	..
i-C_4H_9OH	.693	..	.17	.66	..
$(C_2H_5)(CH_3)CHCH_2OH$	.....	..	.19	..	..
$(CH_3)_3CCH_2OH$	.....	.45	...	..	..
$(CH_3)_2CHOH$	.305	..	.054	.55	26.5
$(CH_3)_2(C_2H_5)CHOH$	.321	..	.04	.53	22.6
$(CH_3)_3COH$	.00318	..	.015	..	1.4
$(CH_3)_2(C_2H_5)COH$	.00728	..	.014	..	.8

the silicon atom than would be the case for similar groups on a carbon atom, as has been pointed out by Whitmore and Sommer.[3] The interaction of the closely packed groups on a carbon atom probably is partly responsible for the inactivity of neopentyl alcohol. The lack of this effect, however, can scarcely explain the enhanced activity of its silicon analog which appears to be more active than any other alcohol. The explanation for the enhanced activity of this compound might be related to the highly electronegative nature of the Me_3SiCH_2-radical as found by Whitmore, Sommer and Bernstein,[3,13] who found that order of certain radicals was as follows: phenyl > Me_3SiCH_2- > Me- > Et- > n-Pr- > (n-Bu-, n-Hex-) > Benzyl > (Me_3CCH_2-, t-Bu-) as determined by the method of Kharasch and Marker.[14] This relationship of reactivity of alcohol to electronegativity of the radical seems to hold true for the normal alcohols but glaring exceptions are noticeable where branching in the alcohol occurs. Thus benzyl, neopentyl and t-butyl radicals are about equal in electronegativity, but the corresponding alcohols are quite different in relative reactivities. The reactivity of an alcohol probably is dependent upon the electronegativity of the radical as well as upon the steric effects of structure and the separation of the two effects is not possible.

Trimethylsilylmethanol dissolves sodium slowly at room temperature with the evolution of hydrogen. A sample (22 g.) containing a small amount of dissolved sodium was found to be unchanged by heating at 175° in a sealed tube for four days. The same sample diluted with a mixture of methanol (4 ml.) and water (0.5 ml.) was heated at 180° for sixteen hours followed by heating at 210° for two hours. No appreciable change was observed.

The alcohol dissolved slowly in boiling 75% potassium hydroxide solution over a period of several hours to form a clear solution from which an infusible combustible gel was precipitated by the addition of acid. Apparently cleavage of silicon–carbon bonds occurred resulting in the production of a polymeric siloxane material upon acidification of the solution.

Trimethylsilylmethanol dissolved clean amalgamated aluminum foil very quickly with the evolution of much heat when a trace of carbon tetrachloride was added to catalyze the reaction.

Summary

The synthesis of trimethylsilylmethanol and a study of its chemical reactivity is reported.

PITTSBURGH, PENNSYLVANIA
RECEIVED SEPTEMBER 2, 1947

---

[10] Norris, Ashdown and Cortese, THIS JOURNAL, **47**, 837 (1925); **49**, 2640 (1927); found these rate constants for esterification of alcohols with p-nitrobenzoyl chloride recalculated on basis of the rate for methanol equal to unity.

[11] Fehlandt and Adkins, *ibid.*, **57**, 193 (1935); Hatch and Adkins, *ibid.*, **59**, 1694 (1937), found relative reactivities from methanolysis studies.

[12] Menschutkin, *Ann. chim. phys.*, [5] **30**, 81 (1883), reacted alcohols with acetic acid one hour at 155°.

[13] Whitmore and Bernstein, THIS JOURNAL, **60**, 2626 (1938).

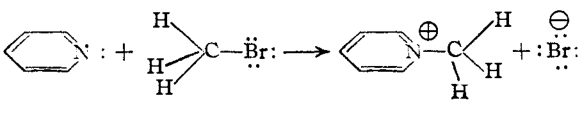
[14] Kharasch and Marker, *ibid.*, **48**, 3140 (1926).

[CONTRIBUTION NO. 1145 FROM THE GATES AND CRELLIN LABORATORIES OF CALIFORNIA INSTITUTE OF TECHNOLOGY AND FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Kinetic Evidence for a Termolecular Mechanism in Displacement Reactions of Triphenylmethyl Halides in Benzene Solution

BY C. GARDNER SWAIN[1]

According to current theory there are only two commonly occurring mechanisms for nucleophilic displacement reactions. One is the bimolecular, kinetically second order (S_N2) substitution or "Walden Inversion."[2] In this mechanism the driving force is exclusively a "push" or *nucleophilic* attack by the entering atom or group, which has an unshared pair of electrons that it is eager to donate in bond formation. The attack is entirely from the back side. An example is the reaction of *primary* halides, such as methyl bromide, with pyridine in benzene solution.

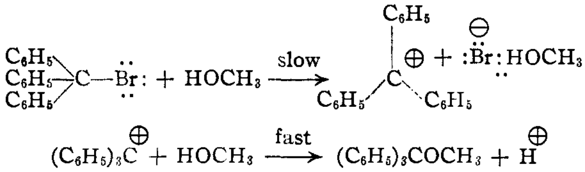


---

[1] National Research Fellow 1945–1946; American Chemical Society Fellow 1946–1947. Paper presented at the New York meeting of the American Chemical Society, September 17, 1947.

[2] (a) Walden, *Ber.*, **28**, 1287 (1895); (b) Lewis, "Valence and the Structure of Atoms and Molecules," 1923, p. 113; (c) Hughes, Juliusberger, Masterman, Topley and Weiss, *J. Chem. Soc.*, 1525 (1935); (d) A. G. Evans, "Reactions of Organic Halides in Solution," Manchester University Press (1946); *Trans. Faraday Soc.*, **42**, 719 (1946).

The other is the ionization (S_N1) mechanism,[3] which dominates for reactions of *tertiary* halides. It is with this second mechanism that the present paper is concerned. According to the most widely accepted interpretation,[3e] the driving force in this case is exclusively a "pull" or front side attack by the solvent or some *electrophilic* solute, which hydrogen bonds with or otherwise solvates the leaving atom or group due to simple electrostatic attraction or to formation of a coördinate bond with the unshared electron pair on the leaving group. This weakens the old bond, allowing it to ionize in the rate-determining step. The reaction is kinetically first order when it is with a solvent which is in large excess. An example is the solvolysis of trityl bromide in methanol solution.



$$(C_6H_5)_3\overset{\oplus}{C} + HOCH_3 \xrightarrow{\text{fast}} (C_6H_5)_3COCH_3 + \overset{\oplus}{H}$$

Previous workers have quite generally used a hydroxylic solvent as the reagent in studying the ionization (S_N1) mechanism, and hence have been unable to determine the kinetic order with respect to the reagent, since it was in large excess and did not change in concentration appreciably during the reaction.

There is a qualitative impression, arising from studies in mixed solvents, however, that more than one molecule of the hydroxylic solvent is involved in the rate determining reaction. Hammett considers that from one to three molecules may hydrogen bond with the halogen atom simultaneously, in a "polymolecular" solvolysis, still involving only attack on halogen. Others have proposed that dimers and trimers of the hydroxylic reagent may be involved. Nearly all are unanimous in declaring that there is no experimental evidence for any attack on carbon by the reagent in the rate-determining step.

By using reactants in low, approximately equivalent concentrations in an inert solvent, benzene, we have been able to determine the kinetic order with respect to all nucleophilic and electrophilic species present. As a model tertiary group we selected triphenylmethyl (trityl) rather than *t*-butyl, to avoid the possibility of elimination of hydrogen halide. The various nucleophilic and electrophilic reagents included tertiary amines, methanol and phenol, separately and in mixtures, with the concentration of each species being independently varied.

Our results indicate that the rate determining ionization step occurs by a termolecular mechanism. The ionization is a result of concomitant or "concerted" solvating attacks on carbon and halogen. Simultaneous attack on both atoms is required to effect any reaction. In the rate-determining step one and only one molecule forms a solvation bond (chiefly ionic) to carbon; similarly one and only one hydroxylic molecule becomes bound by a hydrogen bond (ionic bond) to halogen. The result is always a push–pull termolecular mechanism with exactly third order kinetics.

Data.—Triphenylmethyl (trityl) chloride or bromide (0.1 *M*) reacts with methanol (0.05–0.1 *M*) in dry benzene solution containing a tertiary amine (0.1–0.2 *M*) at 25° to give trityl methyl ether. The tertiary amine is used simply to take up the hydrogen halide formed and render the reaction irreversible. The reaction between trityl halides and tertiary amines is negligibly slow under these conditions, and the rate of the reaction with methanol is unaffected by changing the concentration of tertiary amine used. Triethylamine, a stronger base than pyridine by five powers of ten, gives approximately the same rate as pyridine.

Within experimental error the reaction with methanol is exactly third order (first order in trityl halide, second order in methanol). Rate "constants" calculated assuming that the reaction is second order (first order in each) decrease two-fold within a kinetic run, while third order constants show less than 15% scatter and no trend. Comparing two runs having a two-fold ratio of initial concentration of methanol, the calculated average second order "constants" differ by two-fold; while the average third order constants are the same within 5%. The fact that the order is so precisely third, rather than intermediate between second and third or between third and fourth, suggests that we are dealing with a pure mechanism which accounts for all of the reaction observed.

If phenol is used instead of methanol, the phenyl ether is obtained but at less than one-fiftieth the rate. The reaction appears to be still third order (second order in phenol), although an inverse, roughly first order dependence on pyridine concentration indicates that about half of the phenol is complexed by the pyridine. If the reaction proceeded by an ionization (S_N1) mechanism, one would have expected phenol to bring about a faster reaction than methanol, since it is known to form stronger hydrogen bonds with halogens.[4] The slower reaction of phenol can best be explained by assuming that a solvation of the carbon is required, in which phenol, due to its larger size, would be much less effective than methanol.

---

[3] (a) Ward, *J. Chem. Soc.*, 2285 (1927). (b) Hughes and Ingold, *Nature*, **132**, 933 (1933). (c) Steigman and Hammett, This Journal, **59**, 2536 (1937); Farinacci and Hammett, *ibid.*, **59**, 2542 (1937); **60**, 3097 (1938). (d) Hughes, *Trans. Faraday Soc.*, **37**, 604, 612 (1941). (e) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 54, 172. Solvation of the carbon has generally been considered a negligible contribution to the driving force. However, theoretical arguments for it have been occasionally advanced (*cf.* Winstein and Buckles, This Journal, **64**, 2780 (1942), and Evans, ref. 2d).

[4] Bartlett and Dauben, This Journal, **62**, 1339 (1940) Hantzsch, *Ber.*, **58**, 627 (1925).

When both methanol and phenol are present, only methanol is consumed as long as the methanol lasts. However the rate of reaction is many times faster than in the absence of phenol. The rapid phase of the reaction ends when trityl chloride or bromide equivalent to the methanol present has been consumed. Beyond this point reaction proceeds further at the very slow rate characteristic of runs with phenol alone, until additional trityl halide equivalent to the phenol present has been consumed. An average third order rate constant calculated for the rapid phase of the reaction with trityl chloride in the same way as in the absence of phenol was twenty times larger in the presence of phenol equivalent to the methanol. However this constant increased three-fold within the run, indicating that this kinetic order was incorrect. The reaction was found to be exactly second order within a run (first order in trityl chloride, first order in methanol). However, when runs of different initial concentration of phenol were compared, it was found that the reaction was also first order in phenol, hence again exactly third order over-all. The lack of a kinetic dependence on phenol within a run was evidently due to the fact that phenol was not consumed until all methanol was exhausted. A new third order rate constant, calculated for $dx/dt = k_3'$ (RX) (CH_3OH)(C_6H_5OH), was seven times as large as the old third order constant for runs in the absence of phenol.

This seven-fold acceleration of the rate of reaction of trityl halides with methanol, caused by adding phenol, a substance which reacts only very slowly with trityl halides by itself, is best explained by assuming that a solvation of halogen is also required in these reactions. Phenol is an excellent reagent for solvating halogen, but a very poor one for solvating carbon. Since solvation of both halogen and carbon is required, it reacts very slowly. Methanol is moderate as a halogen reagent, excellent as a carbon reagent, hence reacts moderately rapidly by itself. However, when both are present, each performs independently the function to which it is best adapted and a very high rate results.

The data from typical runs is presented in Tables I and II. Figure 1 shows the course of the reaction of trityl chloride with methanol, phenol, and a mixture of the two. Tables III and IV give detailed data for the more important runs. It is by such tables that all the rate constants of Tables I and II were obtained. The constants are defined as follows. Let

τ = initial moles/liter of trityl halide
μ = initial moles/liter of methanol
ϕ = initial moles/liter of phenol
x = moles/liter of reaction
t = minutes
$Q = \tau/\mu$; $z = x/\mu$

For methanol

$$k_3 = \frac{dx/dt}{(\mu - x)^2(\tau - x)} = \frac{1}{\mu(Q-1)t}\left(\frac{z}{\mu(1-z)} - \frac{2.303}{\mu(Q-1)}\log\left[\frac{Q-z}{Q(1-z)}\right]\right)$$

For phenol the expression is the same except that μ is replaced by ϕ. For methanol and phenol

$$k_3' = \frac{dx/dt}{\phi(\mu - x)(\tau - x)} = \frac{2.303}{\phi\mu(Q-1)t}\log\left[\frac{Q-z}{Q(1-z)}\right]$$

These equations were applied to the data in their integrated rather than in their differential forms to obtain the maximum accuracy.

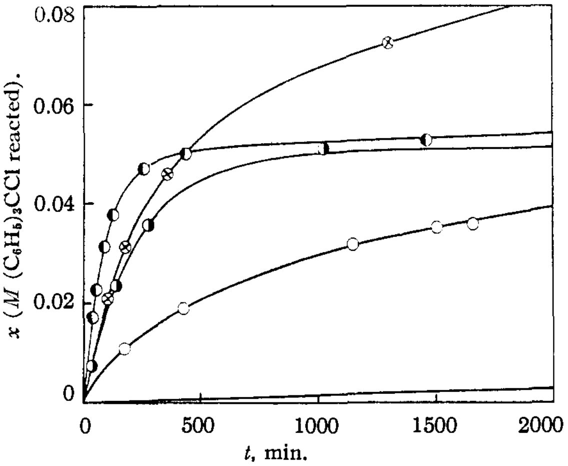


Fig. 1.—Reactions of 0.106 M trityl chloride in dry benzene solution in the presence of 0.108 M pyridine at 25°: lowest line for reaction with 0.056 M phenol; ⊙, 0.054 M methanol; ⊗, 0.109 M methanol; ◑, 0.054 M methanol plus 0.023 M phenol; ◐, 0.054 M methanol plus 0.056 M phenol.

The Salt Effect.—The concentration of dissolved pyridine hydrochloride is five times greater in the presence of phenol than with just methanol (see experimental section on procedure). However, the increased salt concentration caused by the presence of the phenol is not the cause of the greatly increased rate of reaction with methanol. It is true that there is a positive salt effect in this reaction, but it is of small magnitude. It was measured by substituting other tertiary amines having successively more soluble hydrochlorides for the pyridine, and observing the effect on the reaction with methanol in the absence of phenol. Quinaldine is less soluble by a factor of two and gave $k_3 = 0.21$ instead of 0.26. Quinoline is more soluble by a factor of three and gave $k_3 = 0.35$. With diethylaniline the salt dissolved indefinitely, giving $k_3 = 0.25$. A further check on this point was made by substituting quinaldine for pyridine in a reaction with methanol and phenol. In spite of the lower salt solubility, the same seven-fold acceleration was observed.

TABLE I

REACTIONS OF TRITYL CHLORIDE IN DRY BENZENE SOLUTION AT 25°

Run	M $(C_6H_5)_3CCl$	M R_3N	M CH_3OH	M C_6H_5OH	k_2 (l./mole min.)	k_3 (l.^{2}/mole^2 min.)	k_3' (l.^{2}/mole^2 min.)
32, 55	0.106	0.108^a	...	...	<0.000001	....	....
46	.106	.064^a	0.054	...	.0096^e	0.275 ± 0.04	....
50	.106	.108^a	.054	...	.0083^e	.263 ± .04	....
47	.106	.215^a	.054	...	.0088^e	.252 ± .04	....
40	.106	.108^a	.109	...	.0199^e	.252 ± .04	....
48	.106	.103^b	.054	...	....	.21 ± .04	....
51	.106	.108^c	.054	...	....	.35 ± .06	....
49	.106	.107^d	.054	...	....	.25 ± .04	....
54	.064	.108^a	.054	...	....	.21 ± .06^f	....
34, 56	.106	.108^a	...	0.056	....	.004 ± .002	....
43	.106	.108^a	.054	.023	....	1.3^g	1.98 ± 0.3
35	.106	.108^a	.054	.056	....	5.0^g	1.89 ± .3
52	.106	.103^b	.054	.056	....	3.5^g	2.03 ± .4
58	.106	.215^a	.054	.056	....	2.5^g	1.18 ± .2
53	.106	.108^a	.054	.030^h	....	...	4.9 ± .8
60	.106	.108^a	.054	...	....	0.75 ± .12^i	....
59	.075^k	.093^a	.054	...	....	8.0 ± 1.2^k	....

[a] R_3N = pyridine. [b] R_3N = quinaldine. [c] R_3N = quinoline. [d] R_3N = diethylaniline. [e] Not constant. Compare runs 40 and 50, which would have same k_2 if the kinetics were second order. Also note two-fold decrease in k_2 during a run in Table III. [f] Less accurate than constants from other runs due to smaller titers. [g] Not constant. Note three-fold increase in this k_3 during a run in Table IV. [h] Used p-$O_2NC_6H_4OH$ instead of C_6H_5OH. [i] At 56.5° rather than 25°. [k] $(p\text{-}t\text{-}C_4H_9C_6H_4)_3CCl$ rather than $(C_6H_5)_3CCl$.

TABLE II

REACTIONS OF TRITYL BROMIDE IN DRY BENZENE SOLUTION IN THE PRESENCE OF PYRIDINE AT 25°

Run	M $(C_6H_5)_3CBr$	M C_5H_5N	M Addend	Addend	k_2 (l./mole min.)	k_3 (l.^{2}/mole^2 min.)	k_3' (l.^{2}/mole^2 min.)
19	0.103	0.110	...	....	≤0.000002	....	......
10	.098	.108	0.106	$(C_6H_5)_3COH$	....	0.0014^a	......
45	.098	.108	.054	$C_6H_5NHCH_3$	....	.03 ± 0.01	......
21	.103	.220	.032	C_6H_5OH	.00072	.038 ± .006	......
17	.098	.108	.032	C_6H_5OH	.0015	.066 ± .010	......
24	.103	.074	.032	C_6H_5OH	.0018	.081 ± .013	......
20	.103	.110	.190	C_6H_5OH	.027	.178 ± .03	......
22	.103	.110	.037	p-$O_2NC_6H_4OH$	....	.17 ± .03	......
28	.103	.055	.037	p-$O_2NC_6H_4OH$	....	.79 ± .12	......
23	.103	.110	.055	p-$H_3CC_6H_4SH$	....	12 ± 2	......
31	.103	.111^b	.055	CH_3OH	....	18 ± 6^c	......
39	.098	.108	.033	CH_3OH	....	21.9 ± 4	......
26	.103	.220	.055	CH_3OH	....	21.3 ± 4	......
25	.103	.110	.055	CH_3OH	....	23.6 ± 4	......
30	.103	.110	.055 .032	CH_3OH C_6H_5OH	....	200. ± 70^d	90 ± 30^d
27	.103	.110	.054	p-$H_3CC_6H_4NH_2$		Too fast to measure	
18	.103	.110	.011	H_2O			

[a] At 60° rather than 25°. [b] Triethylamine used instead of pyridine. [c] Chloride ion titration necessitated only in this run was not as accurate as hydrogen ion titration used elsewhere. [d] Based on first (nine minute) point. Other points were too close to infinite titer to give accurate results.

One might argue that in the mixed methanol–phenol runs we might have an increased concentration of salt arising not only from the increased solubility of pyridine hydrochloride but also from the association of pyridine and phenol. However the latter type of complex, if it were a salt, should be even less effective electrically than the hydrochloride, because the charges would be buried in the middle of much organic material. To check this, the concentration of pyridine in a mixed methanol–phenol run was doubled, and it was observed, as expected, that the rate constant decreased to 64% of its previous value as a result of the decreased concentration of free phenol, in spite of an increased concentration of the dissolved pyridine–phenol complex.

The Mass Effect.—There is no indication of a mass effect, *i. e.*, of reversal of carbonium ion formation caused by chloride ion accumulating as a reaction product. In the experiments on the salt effect the rate at first showed a steady, though small, increase rather than decrease as the con-

TABLE III

REACTION OF 0.106 *M* TRITYL CHLORIDE WITH 0.054 *M* METHANOL IN DRY BENZENE SOLUTION IN THE PRESENCE OF PYRIDINE AT 25°

Run 46, 0.064 *M* pyridine; run 50, 0.108 *M* pyridine; run 47, 0.215 *M* pyridine. Q = 1.963.

Run	t, min.	x, moles/l.	$x_{cor.}$	z	k_2	k_3
50	20	0.0010	....	...	....	...
47	22	.0003	....	...	....	...
46	22	.0010	....	...	....	...
47	168	.0067	0.0091	0.169	0.0107	0.224
46	174	.0086	.0110	.204	.0127	.278
47	418	.0157	.0181	.335	.0101	.234
50	426	.0165	.0189	.350	.0105	.248
46	444	.0183	.0207	.384	.0115	.278
50	1150	.0294	.0318	.589	.0089	.272
47	1440	.0310	.0334	.618	.0077	.252
46	1510	.0321	.0345	.639	.0080	.264
50	1660	.0330	.0354	.656	.0077	.263
47	2890	.0394	.0418	.774	.0066	.296
46	2900	.0390	.0414	.767	.0064	.281
50	3120	.0392	.0416	.771	.0060	.269
47	193000	.0490	.0514	.952	....	...
					Av. 0.0089	0.263

TABLE IV

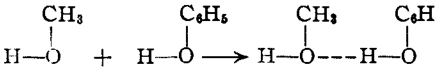
REACTION OF 0.106 *M* TRITYL CHLORIDE WITH 0.054 *M* METHANOL IN DRY BENZENE SOLUTION WITH 0.056 *M* PHENOL AT 25°

Run 35, 0.108 *M* pyridine; run 52, 0.103 *M* quinaldine. Q = 1.963.

Run	t	x	$x_{cor.}$	z	k_3	k_3'
52	21	0.0003	....	...	..	..
35	27	.0003	....	...	..	..
35	39	.0017	0.0172	0.318	2.30	1.82
52	53	.0157	.0227	.420	2.74	1.98
35	55	.0055	.0210	.389	2.30	1.69
35	91	.0159	.0314	.582	3.32	1.97
52	127	.0309	.0379	.702	4.35	2.08
35	203	.0295	.0450	.834	6.55	2.10
35	258	.0315	.0470	.870	7.14	1.93
35	434	.0344	.0499	.924	8.31	1.54
35	1460	.0372	.0527	...	..	..
35	40,500	.0550	.0705	...	..	..
35	57,800	.0577	.0732	...	..	..
52	111,000	.0762	.0832	...	..	..
						Av. 1.89

centration of dissolved tertiary amine hydrochloride was increased by varying the amine used.

Evidence Against a Methanol–Phenol Complex.—Another alternative interpretation of the increased rate of reaction with methanol caused by adding phenol must be ruled out before the picture of simultaneous solvation of carbon by methanol and solvation of halogen by phenol will be on a firm footing. One might interpret the increase by saying that only halogen solvation is involved, but that the solvating agent is a hydrogen bonded complex between methanol and phenol.

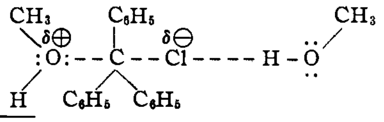


$$\underset{\text{H—O}}{\overset{\text{CH}_3}{|}} + \underset{\text{H—O}}{\overset{\text{C}_6\text{H}_5}{|}} \longrightarrow \text{H—}\overset{\text{CH}_3}{\underset{\text{O}}{|}}\text{---H—}\overset{\text{C}_6\text{H}_5}{\underset{\text{O}}{|}}$$

However, if this view were correct, this complex would have to form an even stronger hydrogen bond to halogen than phenol, to account for the much faster rate than in the case of solvolysis by phenol alone. That no complex having such hydrogen bonding ability exists in appreciable concentration can be shown by measurement of the enhancement of the acidity of hydrogen chloride dissolved in ether caused by methanol, phenol and a mixture of the two.[4] This enhancement depends on and is a measure of the extent of hydrogen bonding of the hydroxylic species with the chlorine of $(C_2H_5)_2O \cdot HCl$. This hydrogen bonding weakens the H–Cl bond and increases the extent of ionization. Evidently the system used for measuring the effect is very similar to our kinetic system where the C–Cl bond of $(C_6H_5)_3CCl$ is being weakened in the same way. Yet the results showed that phenol is much better at hydrogen bonding than methanol, rather than poorer, and that the mixture of the two is no better than the sum of phenol and methanol solutions taken separately. The above experiment argues against the existence of hydrogen bonding between methanol and phenol. The fact that the rate of reaction with methanol is completely independent of pyridine concentration shows that there is less than 15% hydrogen bonding between pyridine and methanol. However, the effect of pyridine concentration on the rate with phenol is probably due to hydrogen bonding.

Other Reagents.—*p*-Nitrophenol is almost entirely associated, probably in a hydrogen bonded complex, by excess pyridine in benzene solution at 25°, as shown by the inverse second order dependence of rate on pyridine concentration in reactions with trityl bromide. However, the small portion which is free, by reason of its great hydrogen bonding ability, is able to increase the overall rate to a higher value than phenol, in spite of the fact that a smaller concentration is acting. The constant k_3', calculated as if all the *p*-nitrophenol were uncombined and effective, is twenty times, rather than seven times, as large as k_3 with just methanol present.

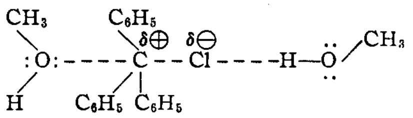
tris-(*p*-*t*-Butyl)-trityl chloride reacts with methanol in dry benzene solution thirty times as rapidly as does trityl chloride. According to Hammett's treatment[5] of the reactions of *m*- and *p*-substituted benzene derivatives, the *p*-*t*-butyl group has a substituent constant of −0.20. This gives a reaction constant of −7.5, or −2.5 per *t*-butyl group, representing a rather high sensitivity of the reaction to substituents. The direction of the change in rate is opposite to what one would expect if stabilization of the transition state



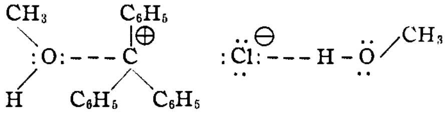
---

(5) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., N. Y., 1940, pp. 118–124, 184–228.

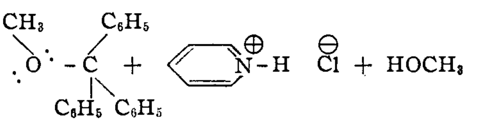
or formation of the covalent bond to oxygen were the most important factors determining the rate. However, it is what one would expect if the transition state were



and if the product formed by the rate-determining step is

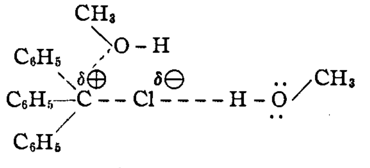


i. e., a solvated ion pair. The bonds with three dashes represent ion-dipole solvation bonds. The solvated ion pair may then react to form the products



in a fast follow-up step or succession of such steps. The methanol molecule which finally reacts, *i. e.*, becomes covalently bonded to carbon in the product determining step is not necessarily the same molecule that solvates the carbon in the rate determining step. The two steps are ***independent***, and our study sheds light on only the rate-determining step. However, in this particular case it is possible that the same methanol molecule is involved in both steps.

We have pictured the solvation of halogen as a ***front side*** attack and the solvation of carbon as a ***back side*** attack. This stereo-relationship seems most likely but is not uniquely consistent with our experimental results. It is conceivable that the molecule solvating carbon may approach from the front side.



We are conducting experiments on displacement reactions of optically active halides in benzene solution which may shed light on the stereochemistry. However, pending further results we favor the picture of back side solvation of carbon.

Table II shows the relative reactivity of a number of different types of compounds toward trityl bromide. This series shows at least two forces at work.

(1) Steric Hindrance.—While methanol reacts very rapidly, triphenylcarbinol does not react detectably. Also pyridine does not react even when there is phenol in the system. Stuart molecular models, which have approximate interference radii, confirm the impossibility of back side collision of the oxygen or nitrogen with the trityl bromide carbon in these cases. On the other hand, phenol has less hindrance, and in the models its oxygen can just be caused to touch the carbon by proper orientation of groups. With methanol this is considerably easier and contact can be achieved with a large variety of orientations. The water molecule has the least steric hindrance of all. The relative rates for these compounds are the ones expected on the basis of these steric considerations.

(2) Basicity of the Atom Solvating Carbon.—On steric grounds *p*-toluidine and *p*-thiocreosol would be expected to react about as slowly as phenol. They are certainly much less hindered than pyridine but no less hindered than phenol. Actually *p*-toluidine reacts immeasurably fast (like water), and thiocresol almost as fast as methanol. We consider that solvation bonds are chiefly ionic in type. However the solvation bonds to carbon might have 25% covalent character, so that differences in nucleophilic tendency of the solvating atom could effect some difference in the rate of reaction. The high "reaction basicity" or nucleophilic character of S is a striking thing, since S is not a basic atom in the usual sense, *i.e.*, when an equilibrium measurement is made involving addition of a proton.

Examination of molecular models indicates that *t*-butyl halides would have the same high degree of back side hindrance as trityl halides, but no experiments were run on *t*-butyl halides.

Termolecular Reactions in Liquid Phase.—The evidence presented indicates that simultaneous solvating attacks on the carbon and halogen are necessary to effect reaction of the trityl halides in benzene solution. The reaction of trityl chloride with methanol has the surprisingly low activation energy of 6.6 ± 1.0 kcal. This means a frequency factor of only 300 $1.^2$/mole^2 sec., or the large negative entropy of activation[6] of −49 ± 4 cal./mole, referred to a standard state of one mole/l., as compared with an activation entropy of about −15 ± 5 cal./mole, referred to the same standard state, calculated for a hypothetical termolecular reaction in the gas phase having a steric factor of unity and hence a frequency factor equal to the termolecular collision rate of 10^{10} $1.^2$/mole^2 sec. This indicates a very precise orientation requirement for reaction, but an energetically very easy reaction path once the proper steric relationships are satisfied.

Third order kinetics have been observed previously in the bromination of olefins,[7] the cleavage of ethers with hydrogen bromide,[8] and the hydrogen chloride catalyzed addition of hydrogen bromide to olefins.[9] These reactions very probably

---

[6] Glasstone, Laidler and Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., N. Y., 1941, p. 199, eqn. 178.

[7] Nozaki and Ogg, THIS JOURNAL, **64**, 706 (1942).

[8] Mayo, Hardy and Schultz, *ibid.*, **63**, 433 (1941).

[9] Maass and Sivertz, *ibid.*, **47**, 2888 (1925).

also involve termolecular mechanisms. They too have abnormally low activation energies.

It is impossible kinetically to distinguish a termolecular reaction from a rapid bimolecular association of two of the reactants to give a low equilibrium concentration of a complex, followed by slow bimolecular reaction of the complex with the third reactant. Thus the rate determining step in our experiments might be a back side attack by methanol on a solvated trityl halide complex, $(C_6H_5)_3CCl$— – – – HOR. In the opinion of the author the distinction between this and a simultaneous back and front side attack, or termolecular reaction, lacks physical significance because the two pictures are so nearly identical. The complex, pictured above, would have a very short lifetime. The making and breaking of bonds between hydrogen and halogen, oxygen, sulfur or nitrogen is never activation controlled, and so cannot be postulated as a slow step in any organic reaction unless the reactants are in exceptionally minute concentration. If the back side attack must follow so quickly after the front side solvation, one might as well call the process a termolecular reaction.

Let us consider a trityl halide molecule and a methanol or phenol molecule which have just diffused together and collided for the first time. They are surrounded by a "cage" of benzene molecules which makes it difficult for them to separate again. Even if there were no attractive force between them, they might undergo a great many repeated collisions, perhaps a thousand or more, with the solvent molecules forming the wall of the cage, and with each other, before one of them would break out of the cage. The existence of a hydrogen bond of 3.0 to 6.0 kcal. strength between the halide molecule and the methanol or phenol will further significantly prolong (by a factor of 150 to 25,000) the period that a pair is associated together in one "encounter."[10] If at any time within this period another methanol or phenol molecule happens to break into the same cage, there is a minute but nevertheless finite probability of reaction, since a sizeable number of termolecular collisions may occur before one of the three molecules breaks out of the cage.

Bringing a new methanol dipole (1.7 Debye units, 1 Å. long) up to the interference distance (2.8 Å.) between oxygen and carbon would contribute 5.5 kcal./mole to the driving force of the reaction if one assumes an internal dielectric constant of 2.0. This added driving force is equivalent to a ten thousand-fold increase in rate, which must evidently outweigh the steric unlikelihood of a termolecular route as compared to a simple bimolecular reaction not involving solvation of carbon.

This double attack (or termolecular mechanism) is closely similar to the effects which were observed by Lowry in the mutarotation of tetramethylglucose.[11] Both an acid and a base appeared to be necessary in that reaction. The rate in a mixture of pyridine and cresol was far greater than that in either solvent alone.

Range of Applicability of this Mechanism.—Thus far the interpretation has been backed by experimental evidence. What follows is an extrapolation of the findings in the one particular system studied to other systems. The generalizations and predictions which follow seem probable now and should be helpful in planning future work, but must be recognized as speculative.

At most we have established this mechanism only for benzene solution, and it is hard to see how we could even go about determining the order with respect to methanol or water in methanol or aqueous solution with certainty. However, it seems inevitable that, as the concentration of hydroxylic reagent is increased, the higher order mechanism involving solvation of both carbon and halogen should still further outstrip a lower order mechanism involving only solvation of halogen. The ease of production of a solvated ion pair should reflect the internal dielectric constant of the halide ($\sim$2?), the polarizability of its electrons, and the specific nature and concentration of the solvating species. It does not seem reasonable to expect a large dependence on the dielectric constant of the medium, since internal dielectric constant should be much more important, and this is a function of only the halide and its two nearest neighbors, *e.g.*, two methanol molecules involved in back and front side solvation. On this view, methanol is not a much different medium than benzene containing 0.1 M methanol, for carrying out halide solvolyses. The large difference in rate is chiefly due to the difference in concentration of methanol in the two cases, although self-association of methanol in the pure solvent may have some small effect on the comparison.

Except for a generally higher reactivity, the situation with water should be similar to the situation with methanol.

Trityl halides are more strongly hindered with respect to attack on carbon than most other halides, yet these experiments indicate that such attack in the form of solvation is still required as part of the driving force which effects reaction. This suggests that attack on carbon is involved in the rate determining step of all displacements on carbon. According to this idea, attack on carbon is always necessary. Attack on the grouping to be displaced is optional; it occurs with tertiary halides; but there are certainly cases where it is not involved among the reactions of primary halides, *e.g.*, the reaction of methyl bromide with pyridine in benzene solution.[12]

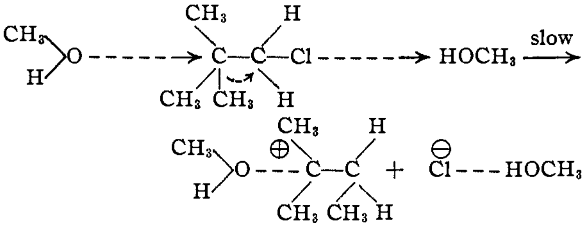
---

(10) Rabinowitz. *Trans. Faraday Soc.*, **33**, 1227, 1229 (1937).

(11) Lowry and Faulkner, *J. Chem. Soc.*, **127**, 2883 (1925).

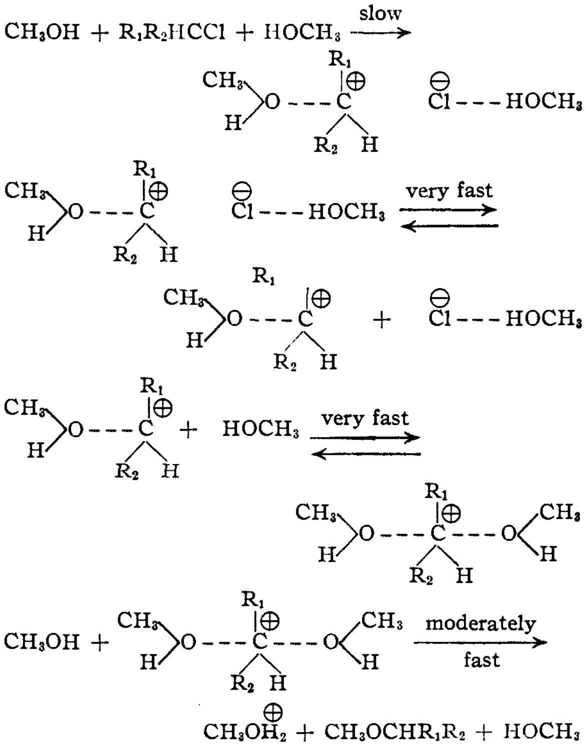
(12) We are neglecting solvation by benzene through van der Waals attractive forces, which, estimated by the heat of vaporization of benzene or methanol, may amount to 8 kcal./mole. This would be important in any comparison with the corresponding reaction run in gas phase. However, halide solvolyses have never been accomplished in homogeneous gas phase, and all real experiments compared in this paper were in liquid phase, for which these van der Waals forces are approximately constant.

The type of attack on carbon involved in the rate determining step may vary. With primary halides it gives a covalent bond; with tertiary halides it is a solvation giving a chiefly ionic or ion-dipolar bond. In other cases the attack on carbon may even be on a different carbon than that from which the leaving group is displaced, as in neopentyl chloride.



Here the whole process including the Wagner–Meerwein shift can be pictured as occurring in one step. Elimination (E_1) and displacement (S_N1) would both involve the same solvated carbonium ion intermediate. If this view is correct, it should be possible to substantiate the requirement of attack on carbon by demonstrating termolecular kinetics as we have done with trityl chloride.

First order racemizations in alcoholic or aqueous solution may be due to rapid formation of a disolvated carbonium ion, facilitated by dissociation of the ion pair in these polar solvents and by the high concentration of hydroxylic reagent present. These two factors would permit the existence of two very fast steps in alcoholic or aqueous solution which would not be probable steps in an inert solvent of low dielectric constant such as benzene.



Failure of hydroxide ion to accelerate the hydrolysis of tertiary halides in an aqueous solution is probably due to the ion's large solvation shell of water, which prevents it sterically from approaching very close to the central carbon.

Experimental

Reagents:—Trityl chloride was prepared from bromobenzene by the procedures of "Organic Syntheses."[13] The acetyl chloride was C. P. reagent grade. The white product was recrystallized from a benzene–pentane solution. All operations were designed to exclude atmospheric moisture. The product was washed with pentane and dried in a vacuum desiccator. The crystals (160 g., m. p. 109–111°) were as coarse as granulated sugar and had a very pale yellow tint. A 0.425 *M* solution in dry benzene was made up by weight, and this was used for kinetic experiments.

Trityl bromide was prepared from tritanol and dry hydrogen bromide gas. It was crystallized several times from benzene, m. p. 153–155°, with a yellow tint. The stock solution in benzene (0.392 or 0.412 *M*) was kept in a desiccator in the cold room at 4° whenever it was not in use.

Pyridine and methanol were reagent grade, dried over Drierite.

Phenol was reagent grade, dried over Drierite and recrystallized from petroleum ether, yielding snow white needles which were dried in a vacuum desiccator and kept protected from atmospheric moisture.

Benzene was thiophene-free reagent grade, dried over sodium wire.

The tris-(*p*-*t*-butyl)-trityl chloride was prepared by Dr. Marvel and his co-workers,[14] was white, and melted with decomposition at 263–266°.

Other reagents were repurified Eastman Kodak Co. chemicals.

Procedure.—Stock solutions of the reagents in dry benzene were kept in Pyrex glass-stoppered bottles in desiccators over potassium hydroxide to protect them from atmospheric moisture. All bottles, pipets and other glassware were dried in an oven at 130°, then packed while hot into a vacuum desiccator and evacuated to 2 mm. to remove surface moisture.

Run 35 is typical of the procedure used. Twenty cc. of benzene, 20 cc. of 0.430 *M* pyridine, 10 cc. of 0.435 *M* methanol and 10 cc. of 0.448 *M* phenol were pipetted into a dry glass-stoppered Erlenmeyer flask. At zero time 20 cc. of 0.425 *M* trityl chloride was added, and the flask thoroughly swirled to give a clear, homogenous solution. Five cubic centimeter aliquot samples were pipetted into each of ten 125 × 16 mm. soft-glass test-tubes which had been drawn out to give a neck 80 × 3 mm., 20 mm. below the lip, for easy sealing. The tubes were sealed off with a microburner and placed in a 25.0 ± 0.02° thermostat within five minutes. Turbidity first appeared after forty minutes. Eight tubes were saved for regular kinetic points, one tube was opened and analyzed after twenty-seven minutes, before any precipitation, to check the initial concentration, and one at 58,000 minutes to measure the total reaction.

The reaction was followed by taking advantage of the fact that pyridine hydrohalides are only very slightly soluble in benzene and precipitate out as the reaction proceeds. A separate sealed tube was used for each point. After filtering out the hydrohalide, the filtrate was shaken with water to hydrolyze the unreacted trityl halide, and the resulting hydrohalic acid titrated with standard sodium hydroxide. The filtration was performed in a special apparatus in an atmosphere of air which had been dried over potassium hydroxide and finally Drierite, and the sealed tube, filtered crystals and filter paper were washed with three 5-cc. portions of dry benzene and the washings

---

(13) Bachmann and Hetzner, "Organic Syntheses," **23**, 98, 100, John Wiley and Sons, Inc., New York, N. Y., 1943.

(14) Marvel, Kaplan and Himel, THIS JOURNAL, **63**, 1894 (1941).

TABLE V

SOLUBILITIES OF TERTIARY AMINE HYDROCHLORIDES IN DRY BENZENE SOLUTIONS AT 25°

M R_3N	R_3N	*M* CH_3OH	*M* Addend	Addend	*M* $R_3N \cdot HCl$	Run
0.108	Pyridine	...	...	....	0.0006	32, 55
.108	Pyridine	0.054	...	....	.0024	46, 47, 50, 59, 60
.108	Pyridine	.109	...	....	.0045	40
.108	Pyridine	.054	1.5	$(C_2H_5)_2O$	.0017	.....
.103	Quinaldine	.054	...	....	.0015	48
.108	Quinoline	.054	...	....	.0071	51
.107	Diethylaniline[a]	.054	...	....	.0033[a]	49
.108	Pyridine	...	0.056	C_6H_5OH	.0121	34, 56
.108	Pyridine	.054	.023	C_6H_5OH	.0060	43
.108	Pyridine	.054	.056	C_6H_5OH	.0155	35, 58
.103	Quinaldine	.054	.056	C_6H_5OH	.0070	52
.108	Pyridine	.054	.030	*p*-$O_2NC_6H_4OH$	.0100	53
.108	Pyridine	.054	.056	C_6H_5OH	.0016[b]	.....

[a] The solubility of diethylaniline hydrochloride in this medium is 0.041. Consequently no salt precipitation occurred during run 49. The figure given refers to quinaldine, which was added as a precipitating agent just before analyses.
[b] Pyridine hydrobromide used instead of pyridine hydrochloride.

added to the filtrate. The filtrate was shaken with 20 cc. of ethanol and 20 cc. of water for five minutes, then with two successive 20-cc. portions of water. The combined lower layers were titrated with 0.0483 *M* carbonate-free sodium hydroxide using three drops of 0.2% brom thymol blue as indicator.

The data on trityl chloride tend to be more accurate because the reaction with methanol could be followed for two days, as compared to the reaction of trityl bromide with methanol which was half over in about ten minutes. On the other hand, pyridine hydrochloride is about ten times as soluble in the media used as pyridine hydrobromide. This is no longer a negligible solubility in some cases, and must be corrected for in the analysis by adding to the molarity calculated from the sodium hydroxide titer a figure equal to the solubility of pyridine hydrochloride in the particular medium used. Fortunately, these solubilities can be directly measured independently, and do not have to be derived from the kinetic data, although the latter derivation is possible and does give agreement with the direct solubility measurements. Only trityl chloride and the ethers which are reaction products were omitted in the solubility measurement, being replaced by benzene. These have much less effect on the solubility than do methanol or phenol in the solution. Replacement of 13% by volume of the benzene by diethyl ether, for example, had almost no effect on the solubility, whereas 0.1 *M* phenol increased it five-fold. The solubility determinations are given in Table V. All the analytical data for the experiments with trityl chloride have been corrected by these directly measured solubility figures, before plotting or obtaining rate constants such as those in Table I. No corrections for solubility were necessary in the trityl bromide runs.

Reaction Products.—No detectable reaction of trityl bromide occurred in fifty minutes in a solution of 0.103 *M* trityl bromide and 0.055 *M* methanol in dry benzene in run 29. The analytical method used here involved adding 15 cc. of benzene and excess pyridine (2 cc. of 0.440 *M* pyridine) to each 5-cc. aliquot at the end of the measured time interval, immediately filtering out any precipitated pyridine hydrobromide, shaking the filtrate with water to hydrolyze trityl bromide, and titrating with sodium hydroxide. Precipitation was uniformly negligible even when six minutes waiting time was allowed before filtering. Evidently in the absence of tertiary amines accumulating hydrogen bromide can cleave the trityl methyl ether formed, and an equilibrium is reached which is very far on the side of the reactants. Although the reaction may be moderately fast, no net reaction is observed because it is reversible.

A very slow irreversible reaction with a half life of about one year was subsequently observed to take place in these same tubes, however, which converted the bromine to a non-ionic, not readily hydrolyzable form, presumably methyl bromide

$$(C_6H_5)_3CBr + MeOH \underset{\text{fast}}{\rightleftarrows} (C_6H_5)_3COMe + HBr$$

$$(C_6H_5)_3COMe + HBr \overset{\text{slow}}{\rightleftarrows} (C_6H_5)_3COH + MeBr$$

The reaction with tertiary amines alone is probably irreversible but very slow. Only 4% reaction occurred between 0.103 *M* trityl bromide and 0.110 *M* pyridine in run 19 in 250,000 minutes (six months). The triethylamine used instead of pyridine in run 31 gave 24% reaction beyond the endpoint with methanol, which was obtained in a day, on waiting a further 250,000 min. The rates of these reactions with tertiary amines are negligible compared to the rates of the other reactions measured in Tables I and II.

This does not mean that the trityl halides cannot be caused to react with tertiary amines under different conditions than those which we have used in our kinetic study. Tritylpyridinium bromide monophenolate, $(C_6H_5)_3C\overset{\oplus}{N}C_5H_5\ \overset{\ominus}{Br}HOC_6H_5$, was actually obtained by mixing and immediately refrigerating 50 cc. of a homogeneous benzene solution of 0.078 *M* trityl bromide, 0.86 *M* pyridine and 0.038 *M* phenol in a Dry Ice-bath for five minutes. Apparently the solvent froze and gave a high local concentration of the three reactants. On warming to 10° a heavy white precipitate was found to be present. This was filtered out and dried in a vacuum desiccator. It was a white, odorless powder, not particularly hygroscopic. The yield was 0.90 g. (theoretical, 0.93 g.), dec. p., 80°. Molecular weight by sodium hydroxide titer using brom thymol blue, 492 (theoretical, 496). Pyridine concentration by hydrochloric acid titration of resulting neutral solution using methyl orange, 16.1% (theoretical, 15.9%) ionic bromide, 16.2% (theoretical, 16.1%). The phenol was shown to be present in quantity equivalent to the bromide by a comparison of bromine uptake by this material and by phenol itself in 1:1 benzene–ethanol solutions. Under these conditions pyridine, trityl bromide, and tritanol did not absorb bromine. The compound was unstable and spontaneously decomposed to a brown material with a strong odor of phenol when allowed to stand at room temperature overnight in a desiccator.

The above compound is interesting in that it probably contains a hydrogen bond between phenol and bromide ion. However, tritylation of pyridine occurs only when the concentrations of reactants are each several molar, never significantly under our kinetic conditions.

Occasionally kinetic points in the runs with methanol, phenol or both were titrated for bromide as well as for hydrogen ion. Agreement within the limits of experimental error was always obtained, demonstrating that the reaction was entirely a solvolysis by the hydroxylic component and not at all the formation of a quaternary ammonium salt.

Pyridine hydrobromide or hydrochloride precipitates out in the usual procedure as the reaction progresses. In the analysis of one of the tubes in run 37 between 0.106 *M* trityl chloride, 0.112 *M* phenol and 0.108 *M* pyridine, the benzene layer, after extraction with alcohol and water and separation of the water layers for titration with sodium hydroxide, was further extracted with dilute sodium hydroxide, then water, and dried over sodium sulfate. The benzene was evaporated and the flask evacuated at 2 mm. for several hours. There was obtained 0.148 g. (83%) of white crystalline *trityl phenyl ether*, m. p. 93–98°. The recorded m. p. is 103°, as contrasted to 282° for the *p*-tritylphenol. The same treatment applied to a tube from run 40 between 0.106 *M* trityl chloride 0.109 *M* methanol and 0.108 *M* pyridine yielded 0.101 g. (70%) of white crystalline *trityl methyl ether*, m. p. 77–79°. The recorded m. p. is 82°.

Enhancement of Acidity of Hydrogen Chloride in Ether by Methanol, Phenol and a Mixture.—The solutions were prepared by adding a total of 2 cc. of various dry benzene solutions to each of a number of 10-cc. samples of a dry ether solution containing 0.001 *M* butter yellow plus enough dry hydrogen chloride gas to turn the indicator from yellow to a very pale yellow orange. The color was measured with a Cenco "Photelometer" (photoelectric colorimeter) using a Corning No. 401 primary green filter, which gave the largest difference between red and yellow solutions of a number of filters tested. The results are presented in Table VI.

TABLE VI

No.	*M* CH_3OH	*M* C_6H_5OH	Color	% transmission
1	...	...	Yellow-orange	100.0
2	0.036	...	Yellow-orange	89
3	.073	...	Yellow-orange	82
4	...	0.037	Orange	57
5	.036	.037	Orange	53.5
6	...	.075	Red	34.5

Acknowledgment.—The author wishes to thank Professors Linus Pauling, Paul D. Bartlett, Saul Winstein and Alwyn G. Evans for criticisms and suggestions which made a major contribution to this work.

Summary

Methanol reacts rapidly with triphenylmethyl chloride or bromide in benzene solution containing excess pyridine at 25° to give the methyl ether. When phenol is used instead of methanol, the phenyl ether is obtained at a slower rate. However, when both are present, the methyl ether is formed at a rate which is seven times as fast as the *sum* of the rates of reaction with methanol or phenol separately. Evidence is obtained to show that this cannot be a salt effect nor due to a complex between methanol and phenol. The kinetics are third order. In the mixed case this means that the rate is proportional to the product of concentrations of methanol, phenol and halide, although the phenol is not consumed in the rapid phase of the reaction.

This indicates that one molecule of alcohol or phenol hydrogen bonds with the halogen atom, weakening its bond to carbon, while another molecule simultaneously solvates the carbon which is becoming a carbonium ion. Phenol solvates halogen better than carbon; the converse is true for methanol. Therefore the concerted, termolecular attack proceeds at a high rate when both phenol and methanol are present and each can play the part to which it is best adapted.

The relative reactivity of a number of types of compounds toward triphenylmethyl bromide in benzene solution has been measured.

CAMBRIDGE, MASS. RECEIVED AUGUST 11, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

The Chemical Properties of Elements 94 and 93

BY GLENN T. SEABORG AND ARTHUR C. WAHL[1a,b]

This report describes the chemical experiments which we have performed on elements 94 and 93 and the chemical properties which we have deduced from these experiments.

Although these chemical experiments have been under way for 94 since December, 1940, when element 94 was discovered,[2] and for 93 since somewhat earlier than this, the investigation has not been a very systematic one. In the case of element 93, we have repeated most of the experiments reported by McMillan and Abelson[3] in their original publication and have confirmed their results. It has been of paramount importance to develop as quickly as possible methods of isolating in very thin precipitates elements 94 and 93 from large amounts of uranium in order to study the properties of 94^{239},[4] and, therefore, the experiments have been of a very practical and explora-

---

(1a) Now at Department of Chemistry, Washington University, St. Louis, Missouri.

(1b) This article was mailed as a secret report from Berkeley, California, to the "Uranium Committee" in Washington, D. C., on March 21, 1942. The experimental work was done throughout all of 1941 and the early part of 1942. Part of the original material is omitted in order to shorten the article to Journal length; otherwise it is unchanged from its original report form except for slight editing to make it conform to JOURNAL standards.

(2) G. T. Seaborg, E. M. McMillan, J. W. Kennedy, and A. C. Wahl, *Phys. Rev.*, **69**, 366 (1946) (submitted January 28, 1941); G. T. Seaborg, A. C. Wahl and J. W. Kennedy, *ibid.*, **69**, 367 (1946) (submitted March 7, 1941).

(3) E. M. McMillan and P. H. Abelson, *Phys. Rev.*, **57**, 1185 (1940).

(4) J. W. Kennedy, G. T. Seaborg, E. Segrè and A. C. Wahl, *Phys. Rev.*, **70**, 555 (1946) (submitted May 29, 1941).