[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Concerted Displacement Reactions. II. Termolecular Displacement Reactions of Methyl Halides in Benzene Solution[1]

BY C. GARDNER SWAIN AND RICHARD W. EDDY

According to current theory there are two commonly occurring mechanisms for nucleophilic displacement reactions at a saturated carbon atom. The first paper of this series dealt primarily with the one of these which has been variously called unimolecular, polymolecular, solvolytic, electrophilic, first order, and S_N1 by different investigators. For reasons which will become apparent below, as a result of new evidence, each of these names now has confusing and misleading connotations. This mechanism is a *two-step* process involving a solvated, ionic, carbonium salt intermediate. Hence in the present paper we shall refer to it as the *carbonium ion* mechanism.

The other mechanism has been variously called the Walden inversion, the bimolecular, nucleophilic, inverting, second order, and S_N2 mechanism by different authors. It is a simple *one-step* process. In this paper we shall, therefore, call it the *direct* mechanism of displacement.

In the carbonium ion mechanism the primary attack is generally considered to be on only the leaving atom or group, and the driving force to be the affinity of electrophilic solvent or solute molecules for the leaving group. On the other hand, in the direct mechanism the attack is generally considered to be only on carbon, and the driving force to be the affinity of the nucleophilic reagent for carbon.[2]

However, we have shown in the first paper of this series that triphenylmethyl (trityl) halides, which react by the carbonium ion mechanism, undergo displacements in benzene solution requiring in the rate-determining step both pull on the leaving group and attack on carbon, *i.e.*, by a "concerted," push-pull or termolecular process. The product of this termolecular rate-determining step is an ion-pair with both halide ion and carbonium ion solvated. In this paper it will be demonstrated that methyl halides, which are generally considered to react by the direct mechanism, also undergo termolecular displacements in benzene solution requiring in one step both pull on the leaving group and attack on carbon. Although we used only benzene as a solvent in these studies, there is no apparent theoretical reason why the mechanisms should be less concerted in alcohol or water solution. There are indications in the literature that concerted reactions are quite common (see section below on related work).

Data.—We used benzene as solvent rather than alcohol or water, because the existence of a concerted mechanism is experimentally easier to demonstrate in an inert solvent. It was expedient experimentally to study the reaction between methyl bromide and pyridine, which proceeded at a convenient rate, rather than the reaction with methanol, since the latter was slower by five powers of ten. In the case of trityl bromide we previously studied only the reaction with methanol, because it was faster than the reaction with pyridine by six powers of ten. We do not believe that the difference in reagent used alters the conclusions reached or interferes with a comparison of mechanism in the two cases.

Methyl bromide was allowed to react with pyridine in benzene solution both alone and in the presence of substances effective at solvating halide ions, such as methanol, phenol, *p*-nitrophenol, mercuric bromide and aluminum bromide. At 100° the reaction of methyl bromide with pyridine alone in benzene is second order with a rate constant of 2.89 ± 0.15 l./mole min. and an activation energy of 14 ± 0.5 kcal. Methanol (0.10 *M*) increases the rate of reaction of methyl bromide (0.10 *M*) with pyridine (0.10 *M*) by 13 ± 7%; 0.11 *M* phenol increases it 42 ± 9%; 0.055 *M* *p*-nitrophenol 64 ± 10%; 0.11 *M* *p*-nitrophenol 104 ± 12% (twofold); 0.045 *M* mercuric bromide fourfold; 0.044 *M* aluminum bromide 20 ± 8%.

TABLE I

REACTION OF 0.0978 *M* METHYL BROMIDE WITH 0.0993 *M* PYRIDINE IN DRY BENZENE SOLUTION AT 100°

Run No.	Added reagent	Concn. (*M*)	10^2k_2[a] (l./mole min.)
3	None	...	2.89
4	Pyridine	0.199 (total)	2.89
5	Methanol	.098	3.26
6	Phenol	.112	4.11
15	*p*-Nitrophenol	.055	4.75[f]
8	*p*-Nitrophenol	.110	5.90[g]
9	Mercuric bromide	.045	11.5[b]
13	Aluminum bromide	.044	3.50[a]
14	Aluminum bromide	.071	20[e]
1	None	...	0.025[c]
2	None	...	.065[c,d]

[a] The second-order rate constant is calculated as if there were no added reagent, *i. e.*, assuming all the pyridine to be free, except in run 13 with aluminum bromide, where 0.044 *M* inert complex is assumed. [b] This constant holds for only first 50% reaction with average deviation of 11% for five points. Thereafter, it sharply falls to 6.5 at 54%, 4.8 at 67%, 1.9 at 85%. [c] At 25° rather than 100°. [d] Methyl iodide (0.103 *M*) instead of methyl bromide. [e] No pyridine present in this run. [f] Methyl bromide 0.0793 *M* and pyridine 0.0987 *M* in this run. [g] Pyridine 0.0983 *M* in this run.

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[1] The first paper of this series was published in THIS JOURNAL, **70**, 1119 (1948), under the title, "Kinetic Evidence for a Termolecular Mechanism in Displacement Reactions of Triphenylmethyl Halides in Benzene Solution."

[2] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 172.

Table I gives average second-order rate constants for typical kinetic runs. Tables II–V give detailed data for the more important runs. The average deviation of rate constants calculated for each point of a run was always less than 5%, except in run 9 with mercuric bromide.

TABLE II

REACTION OF 0.0978 M METHYL BROMIDE WITH 0.0993 M PYRIDINE IN DRY BENZENE SOLUTION AT 100°; RUN 3; TITER BLANK, 0.4 CC.

Min.	Net cc. 0.0259 N $Hg(NO_3)_2$	% Reaction	10^2k_2
108	4.40	23.3	2.86
159	5.95	31.5	2.90
247	7.85	41.6	2.91
360	9.85	52.2	3.04
453	10.55	55.9	2.79
1370	14.70	77.9	2.52
1460	15.45	81.9	3.26
3250	17.10	90.6	2.80
44700	18.70	98.0	..
			Av. 2.89

TABLE III

REACTION OF 0.0978 M METHYL BROMIDE WITH 0.0993 M PYRIDINE IN DRY BENZENE SOLUTION WITH 0.112 M PHENOL AT 100°; RUN 6; TITER BLANK, 0.4 CC.

Min.	Net cc. 0.0269 N $Hg(NO_3)_2$	% Reaction	10^2k_2
111	5.65	29.9	3.86
245	9.70	51.4	4.32
377	11.63	61.6	4.24
1380	15.90	84.3	3.76
2860	17.55	93.0	4.26
3270	17.70	93.8	4.19
34700	18.90	99.2	..
			Av. 4.11

TABLE IV

REACTION OF 0.0793 M METHYL BROMIDE WITH 0.987 M PYRIDINE IN DRY BENZENE SOLUTION WITH 0.055 M p-NITROPHENOL AT 100°; RUN 15; TITER BLANK 0.4 CC.

Min.	Net cc. 0.0269 N $Hg(NO_3)_2$	% Reaction	10^2k_2
75	3.93	26.7	4.74
131	5.83	39.6	4.76
184	7.10	48.2	4.70
278	9.10	61.7	5.10
394	10.00	67.8	4.54
1368	13.66	92.7	4.70
			Av. 4.75

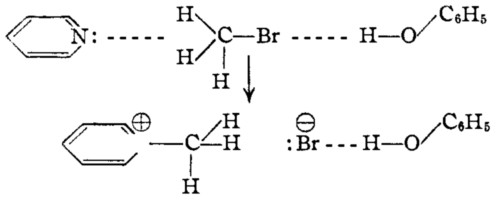
TABLE V

REACTION OF 0.0978 M METHYL BROMIDE WITH 0.0983 M PYRIDINE IN DRY BENZENE SOLUTION WITH 0.11 M p-NITROPHENOL AT 100°; RUN 8; TITER BLANK, 0.4 CC.

Min.	Net cc. 0.0258 N $Hg(NO_3)_2$	% Reaction	10^2k_2
6	0.68	3.6	6.16
16	1.66	8.8	6.35
34	2.95	15.6	5.57
74	5.52	29.1	5.62
101	6.80	35.9	5.49
149	8.47	44.7	5.54
200	10.07	53.2	5.75
276	11.90	62.8	6.19
348	12.80	67.6	6.05
428	13.55	71.5	5.94
1890	17.45	92.1	6.19
			Av. 5.90

The reaction of methyl bromide (2.6 M) with methanol (24.7 M) in the absence of pyridine is very slow; at 25° the second order rate constant is five powers of ten less than the rate constant with pyridine. In the presence of pyridine the product is almost exclusively methylpyridinium bromide since the sodium hydroxide titer (for hydrogen ion) is zero within experimental error (±5%) when the mercuric nitrate titer (for bromide, ±2%) is over 90% in each of the runs with methanol, phenol and p-nitrophenol. None of these hydroxy compounds complex with pyridine in solution at 100° (see experimental section). The product, methylpyridinium bromide, starts to precipitate out immediately, before 2% reaction in all cases.

Added methanol, phenols, or mercuric bromide facilitate reaction, apparently by solvating the bromine atom of methyl bromide in front while pyridine simultaneously attacks from the back side.



A concerted, push-pull, third order mechanism has been superimposed on the ordinary, slower, second order mechanism which must operate in the absence of solvating agents more effective than the solvent, benzene.

If the concentration of p-nitrophenol is varied, the rate of reaction between methyl bromide and pyridine varies in the manner which would be predicted for a third-order reaction superimposed on the second-order reaction occurring in the absence of phenol. That is, the rate in excess of the standard rate is proportional, within experimental error, to the concentration of p-nitrophenol, as well as to the concentrations of methyl bromide and pyridine. We have continued to express the rate by second order rate constants because the phenol is not consumed (the methylpyridinium bromide formed precipitates out as a simple salt without p-nitrophenol of crystallization at 100°); hence, within a given run the kinetics can be treated as second order. However, by comparing two different runs, 8 and 15, the increase in second order constant is seen to be proportional to the initial concentration of p-nitrophenol, thus demonstrating the true third-order nature of the kinetics and the termolecularity of the reaction.

As an alternative, one might try to interpret the increased rates as due to a general medium or solvent change due to the addition of the methanol or phenols, which would cause an increase in the dielectric constant. Reactions of this type do in general go faster in solvents of high dielectric constant. Thus Norris and Prentiss[3] found that the rate of reaction of ethyl bromide with pyridine at 25°, although only 11% faster in *n*-propyl alcohol ($\epsilon = 20$) as a solvent than in benzene ($\epsilon = 2.2$), was increased 2.5-fold in pure methanol ($\epsilon = 32$), 13-fold in acetone ($\epsilon = 21$) and 25-fold in nitrobenzene ($\epsilon = 35$). Similar series were obtained earlier for the reaction of triethylamine and ethyl iodide at 100° by Menschutkin.[4]

However, if one interpolates to find the expected medium effect due to dielectric constant change, the change expected on addition of 0.1 *M* methanol is only a 1% increase in rate, and the change for 0.1 *M* phenol should be even less because phenol has a slightly lower dipole moment and much lower dielectric constant than methanol. These calculated medium effects are negligible because benzene is still in more than a hundred-fold excess over the hydroxy compound so that the medium is essentially unchanged. Actually, a 13% increase in rate is observed with methanol, 42% with phenol, and 104% with *p*-nitrophenol. Evidently, a general medium effect cannot explain this, and the increased rate must be due to a termolecular mechanism.

The solubility of the product, methylpyridinium bromide, is very low in all the solutions studied. Even in the presence of 0.1 *M* *p*-nitrophenol it is less than 0.002 *M* at 100°. Hence it is not likely that dissolved solvated salt molecules participate in the termolecular reaction, but it is probably the hydroxy compounds themselves which participate.

With mercuric bromide a sharp decrease in rate was observed beyond 50% reaction, suggesting that mercuric bromide complexes with methylpyridinium bromide to form methylpyridinium tribromomercurate, effectively removing the mercuric bromide from solution beyond this point. To prove this, the precipitate formed up to 60% reaction was filtered out from one of the tubes in run 9. Titration of the precipitate with mercuric nitrate indicated 13.3% bromide (theor. 15.0%) and Dumas analysis for nitrogen gave 2.68% (theor. 2.62%).

Aluminum bromide is ineffective, probably because it complexes with the pyridine,[5] effectively removing the latter from the solution and being degraded to an inactive form in the process.

Related Work by Other Investigators.—Various concerted, termolecular reactions in the literature were mentioned in the previous paper.[1] They included mutarotation of glucose, bromination of olefins, cleavage of ethers by hydrogen bromide and addition of halogen acids to olefins. In addition, the E2 mechanism of elimination has been shown to be concerted by Skell and Hauser,[6] in the sense that chloride ion is lost at the same time as the β-hydrogen. Simultaneous attacks by alcohol and alkoxide ion, respectively, on these two atoms are probably involved. Second order eliminations are generally *trans*,[7] and this may often be due to the necessity for simultaneous attack on two adjacent centers, which would be sterically hindered if both reagents attacked from the same side.

The alkaline hydrolysis of silanes has been shown to be a termolecular, third-order reaction.[8]

Price has observed that *trans*-2-phenylcyclohexanol is dehydrated by acid to 3-phenylcyclohexene, whereas the *cis* isomer is dehydrated to 1-phenylcyclohexene under the same conditions.[9] Since different products are formed, there cannot be a common carbonium ion intermediate. There must be a concerted attack both on hydroxyl and on an α-hydrogen in at least one of these cases.

Bartlett has found that *cis*-1,2-dimethylcyclohexane-diol-1,2 undergoes the pinacol rearrangement to give 2,2-dimethylcyclohexanone-1, whereas the *trans* isomer yields 1-methyl-1-acetylcyclopentane.[10] Hence the methyl group or ring (depending on which is in back) must shift simultaneously with departure of the hydroxyl group as a water molecule. Wagner–Meerwein rearrangements in general may be concerted processes in this way.

All examples of neighboring group participation have the elements of a concerted or push-pull mechanism. The neighboring group contributes, to a variable extent, to the driving force of the reaction by an internal back side attack on carbon while the solvent or some added reagent solvates the leaving group on the front side.[11]

Termolecular Displacement Reactions.—Concerted, push-pull, termolecular displacements evidently occur not only with a tertiary compound like trityl bromide, which is recognized to react only by the carbonium ion mechanism, but also with methyl bromide, where the mechanism is generally considered to be totally direct. We believe that, in general, nucleophilic displacements of anions from saturated carbon atoms are concerted, require both types of driving force (solvation of the leaving group and attack on carbon) in the one rate determining step, and hence are at least termolecular (*i.e.*, never unimolecular nor bimolecular).[12]

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[3] Norris and Prentiss, THIS JOURNAL, **50**, 3042 (1928).

[4] Menschutkin, *Z. physik. Chem.*, **6**, 41 (1889).

[5] Müller and Wersitsch, *Z. anorg. allgem. Chem.*, **208**, 304 (1932); *Z. Elektrochem.*, **38**, 227 (1932).

[6] Skell and Hauser, *ibid.*, **67**, 1661 (1945).

[7] Cristol, *ibid.*, **69**, 338 (1947).

[8] F. Price, *ibid.*, **69**, 2602 (1947).

[9] C. C. Price and Karabinos, *ibid.*, **62**, 1159, 2243 (1940).

[10] Bartlett and Pöckel, THIS JOURNAL, **59**, 820 (1937).

[11] Winstein and Grunwald, *ibid.*, **68**, 536 (1946).

[12] "Termolecular" refers to mechanism and is not to be confused with kinetic "order," which is the experimentally observed de-

Kinetic order has been used more than any other kind of evidence as proof of the duality of mechanism in nucleophilic displacements at a saturated carbon atom and as a criterion for deciding which mechanism (carbonium ion or direct) holds in a particular case. However, the kinetic order does not depend on mechanism but only on the *degree of participation of the solvent.* Trityl chloride alone in water gives first order kinetics (both attack on carbon and solvation of chlorine by the solvent); benzyl chloride with mercuric nitrate in water solution gives second order kinetics[13] (attack on carbon by solvent and solvation of chlorine by mercuric nitrate); and trityl chloride with methanol and phenol in benzene solution is third order (attack on carbon by methanol, solvation of chlorine by phenol, no participation by solvent). These are all examples of the carbonium ion mechanism. On the other hand the same variation exists among reactions proceeding by the direct mechanism. Methyl bromide alone in water solution gives first order kinetics (both attack on carbon and solvation of bromine by the solvent water); methyl bromide with pyridine in benzene solution is second order (attack on carbon by pyridine and solvation of bromine by the solvent benzene); and methyl bromide with pyridine and mercuric bromide in benzene solution is third order (attack on carbon by pyridine and solvation of bromine by mercuric bromide, no participation by solvent). Evidently, determination of kinetic order can no longer be considered a criterion of mechanism.

The rate of hydrolysis of isopropyl chloride in aqueous alkali involves two terms.

$$-\frac{d[\text{i-PrCl}]}{dt} = -\frac{d[\text{OH}^{\ominus}]}{dt} = k_2[\text{i-PrCl}][\text{OH}^{\ominus}] + k_1[\text{i-PrCl}]$$

The first term has been interpreted as due to the fraction of the halide molecules which are reacting with hydroxide ion by the direct mechanism, the second term to the rest of the molecules reacting with hydroxide ion by the carbonium ion mechanism.[14] We interpret this kinetic complexity rather as merely a competition for isopropyl chloride by two different carbon-attacking reagents, hydroxide ion and water, the chlorine being solvated by water in each case. It may or may not represent a significant difference in mechanism.

The rate of methanolysis of benzhydryl bromide in nitrobenzene solution involves two terms.[15]

$$-\frac{d[(C_6H_5)_2CHCl]}{dt} = +\frac{d[CH_3OH_2^{\oplus}]}{dt} = k_2[(C_6H_5)_2CHCl][CH_3OH] + k_3[(C_6H_5)_2CHCl][CH_3OH]^2$$

We interpret this again as representing merely two different sets of reacting species, not necessarily two mechanisms. The first term represents reaction involving attack on carbon by methanol and solvation of chlorine by the solvent nitrobenzene. The second term represents reaction with both attack on carbon and solvation of chlorine by methanol.

Actually, it appears that kinetic order, the total number and type of reacting molecules, the push-pull character of their attack in the rate determining step, the salt effect, and the effect of change of medium *may all be identical* for such extreme cases as the reactions of trityl and methyl halides. Hence, even taken collectively, these observations cannot be considered as constituting an iron-clad criterion of mechanism, or as showing that there is a difference of kind in the rate-determining steps in the two cases as is currently assumed.

In view of the similar behavior of trityl and methyl halides in benzene solution (and general breakdown in this solvent of the criteria set up by Hughes and Ingold for deciding which mechanism is operative) we prefer to say that there is only one mechanism for displacements of anions from trityl, *t*-butyl, benzyl or methyl compounds by the attack of electrically neutral molecules (water, alcohols or amines) regardless of the kinetic order observed.

The Solvation of the Leaving Group.—We now believe that solvation of the leaving group is required in all nucleophilic displacements of anions from saturated carbon atoms. The most effective solvation is one leading quickly to the formation of a (coördinate) covalent bond (*e. g.*, by mercuric bromide). Next most effective is a solvation exerted through ionic (*e. g.*, hydrogen) bonding (*e. g.*, by phenols). But, if the system is so unfavorably constituted that even this is impossible, polarizable solvent molecules, even if they are only benzene, can always exert a polarization solvation for the leaving group. At short distances the polarization forces are very strong. Judging from the heat of vaporization, this attraction may amount to 7 kcal. Hence even the reaction of methyl bromide with pyridine in pure benzene solution would be termolecular, although kinetically of the second order because the solvent is in large excess. Evidence that the solvent ben-

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pendence of rate on concentration. A termolecular mechanism may exhibit first, second, or third order kinetics depending on the degree of participation of the solvent as two, one or none of the three molecules. The picture of a simultaneous termolecular reaction between three molecules is kinetically indistinguishable and physically not significantly different from one involving very rapid, reversible formation of a low equilibrium concentration of a complex between two of the molecules accompanied by slow reaction of the complex with the third molecule.[1] Strictly speaking, the special case where there is intramolecular attack by a neighboring group in the same molecule is less than termolecular, and hence an exception, but it does not differ fundamentally from the termolecular reactions. It now appears possible to us that there may be a few rare exceptions in which attack on carbon by a separate molecule is not required in the rate determining step, *e. g.*, when there is very high B-strain or strain in the bond angles on carbon in the ground state which is relieved in the transition state.

(13) I. Roberts and Hammett, THIS JOURNAL, **59**, 1063 (1937). Reaction undoubtedly proceeds by the carbonium ion mechanism because a *p*-methyl substituent strongly accelerates the rate (*cf.* Bennett and Jones, *J. Chem. Soc.*, 1815 (1935)).

(14) Hughes, *Trans. Faraday Soc.*, **37**, 606-607, 612-613 (1941)

(15) Bartlett and Nebel, THIS JOURNAL, **62**, 1345 (1940).

zene is solvating the bromine is found in the fact that never has this reaction, nor in fact any nucleophilic displacement reaction, been carried out in homogeneous gas phase. In solution in hexane or cyclohexane, where the resemblance to the gas phase is strong due to very weak polarization forces, this reaction will not occur except heterogeneously on the wall of the containing vessel or on the surface of precipitated crystals.[16]

The Attack on Carbon.—Initially, an attack on carbon is merely the formation of an ionic dipole–dipole bond. This kind of ionic attack on carbon has previously not been adequately considered as a possibility. A pure carbon solvation bond can form immediately with no more delay than the time necessary to move two molecules close together. It is a simple calculable force obeying Coulomb's law, of the same type as the hydrogen bond which solvates the leaving group when hydroxylic solvents are used. This ionic solvation makes it easier for the old covalent bond to break. The molecule solvating carbon may subsequently form a covalent bond, but *this changeover from an ionic bond to a covalent bond to carbon is a slow process.*

About the only experimental difference one can discern between methyl halides and tertiary halides results from a quantitative difference in the rate of this changeover. With methyl halides it may occur with so little lag after the breaking of the old covalent bond that the intermediate "carbonium salt" state may have a total (counting fractional bonds) of nearly four covalent bonds and only a minute fraction of a unit positive charge on carbon. With tertiary halides the carbonium ion has two chiefly ionic bonds, and is relatively "free" and long-lived. In this tertiary case, the carbon-solvating reagent or solvent not only does not become largely covalently bonded in the rate determining step but does not necessarily become so bonded even in the subsequent product determining step: other molecules may become covalently bonded instead, or eliminations, racemizations or rearrangements may occur. This is only a quantitative difference in freedom of the carbonium ion, hardly one of kind.

Experimental

Reagents.—Dow methyl bromide (99.5%) was purified by passing through sulfuric acid wash towers and condensing the vapors in a trap cooled by a Dry Ice–acetone-bath. A stock solution was made by distilling this methyl bromide and passing the gas through benzene until a 2.6 *M* solution was obtained. A 0.391 *M* solution in dry benzene was made up by dilution and this was used for the kinetic experiments.

Pyridine and methanol were reagent grade, dried over Drierite.

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

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.

p-Nitrophenol was a recrystallized Eastman Kodak Co. chemical.

Aluminum bromide was Eimer and Amend reagent grade.

Mercuric bromide was Mallinckrodt analytical reagent.

Procedure.—Stock solutions of the reagents in dry benzene were kept in Pyrex glass-stoppered bottles. All apparatus was dried in an oven at 110° before using.

The procedure during a run can be illustrated by run no. 3. Twenty cc. of 0.397 *M* pyridine and 40 cc. of benzene were pipetted into a dry Erlenmeyer flask. Twenty cc. of 0.391 *M* methyl bromide was added and the flask thoroughly swirled to give a clear, homogeneous solution. Five-cc. samples were pipetted into each of thirteen 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 100.0 ± 0.5° steam thermostat. The time of placing in the bath was recorded as zero time, as the time lag in heating the samples was approximately compensated by the time during which the tubes were at room temperature. One sample was opened and analyzed after 44700 minutes to measure the total reaction. The remaining tubes were saved for regular kinetic points.

The contents of each tube were poured into a 125-cc. separatory funnel and each tube was washed three times with benzene and water; after shaking, the water layer, which contained the dissolved methylpyridinium bromide, was drawn off. After a second extraction with water the combined water layers were titrated with standard mercuric nitrate according to the procedure of Roberts.[17]

The only deviation from this procedure was in the runs with aluminum bromide, where the tubes were made up by the addition of 1 cc. of the methyl bromide solution, 1 cc. of pyridine solution, 1 cc. of benzene and finally 1 cc. of the aluminum bromide solution.

The percentage reactions in the tables are calculated using as 100% the end-point calculated from the initial quantity of methyl bromide used. The concentration of the methyl bromide stock solutions was determined by reaction of aliquot samples with pure pyridine for a long period of time and titration by the same method as in the kinetic runs. All points taken immediately after placing the tubes in the thermostat gave a net titration of 0.00 ± 0.10 cc., indicating 0.0 ± 0.5% reaction.

Solubility of Methylpyridinium Bromide.—The product which precipitates out in the runs with added *p*-nitrophenol at 100° is methylpyridinium bromide. At temperatures below 72° the precipitate contains also *p*-nitrophenol of crystallization, but we avoided making kinetic measurements at temperatures below 72° where this occurred. Precipitation at 100° begins immediately (before 2% reaction) even in the runs with *p*-nitrophenol added. This indicates an upper limit of 0.002 *M* for the solubility of methylpyridinium bromide in our kinetic solutions.

Complexes between Pyridine and Phenols in Benzene Solution.—Phenol or *p*-nitrophenol (0.1 *M*) appears to form hydrogen bonded complexes with pyridine (0.1 *M*) in benzene solution at 5 or 25°. However, these complexes appear to be quantitatively dissociated at 80 or 100°. The instability constant of the *p*-nitrophenol–pyridine complex is 5×10^{-3} at 5°; its formation is exergonic by 3 kcal. but exothermic by more than 9 kcal. These values were calculated from the following data.

A solution of 0.0583 *M* pyridine in benzene depressed the freezing point 0.355°; a solution of 0.0462 *M* pyridine and 0.0517 *M* *p*-nitrophenol measured immediately afterward gave a depression of 0.383°. A solution of 0.100 *M* pyridine in benzene solution elevated the boiling point in a Cottrell boiling point apparatus by 0.185°; a solution of 0.091 *M* pyridine and 0.100 *M* *p*-nitrophenol immediately afterward raised it a total of 0.355°. From these figures we calculate that the pyridine in the second solution was 76 ± 5% in the form of complex at 5°; and

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[16] Pickles and Hinshelwood, *J. Chem. Soc.*, 1354 (1936); Moelwyn-Hughes and Hinshelwood, *ibid.*, 231 (1932).

[17] I. Roberts, *Ind. Eng. Chem., Anal. Ed.*, **8**, 365 (1936).

that the pyridine in the fourth solution was 0 ± 5% in the form of complex at 80°.

These observations are in accord with the first paper in this series, where there were indications that pyridine complexes partially with phenol and fairly completely with *p*-nitrophenol at 25°; also with the present work there is no indication of complexing with these reagents at 100°.

Summary

Methyl halides, as well as triphenylmethyl halides, undergo concerted, termolecular displacements in benzene solution, requiring in the rate-determining step both pull on the leaving group and attack on carbon. The reaction of methyl bromide with pyridine in benzene solution is accelerated several fold by adding 0.05 M concentrations of *p*-nitrophenol or mercuric bromide which are more effective than the solvent benzene at solvating bromine. The effect is too large to be due to a general medium change. The kinetics are third order.

There is no apparent reason why these mechanisms should be less concerted in alcohol or water solution. A survey of the literature reveals that concerted, termolecular mechanisms are remarkably common. It is probable that nucleophilic displacements of anions from saturated carbon atoms are generally of this type, although they may often be cleverly camouflaged because the solvent functions as one (or two) of the three participating molecules.

A displacement proceeding by the carbonium ion mechanism can be kinetically first, second, or third order depending only on the degree of participation of the solvent. A displacement currently considered to proceed by the direct mechanism can also have any of these kinetic orders. The kinetic order or even the total number or type of reacting molecules involved can no longer be considered a criterion of mechanism.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF EMORY UNIVERSITY]

Ultrasonic Velocity in Some Liquid Fluorocarbons[1]

BY R. T. LAGEMANN, W. E. WOOLF, J. S. EVANS AND N. UNDERWOOD[2]

A rather thorough search of the literature reveals that no ultrasonic velocities have been reported for any liquid compound containing fluorine. A similar scarcity of information on ultrasonic velocity exists for liquid polymers—only two studies[3,4] having been made. It was therefore thought to be of interest to measure the velocity of sound in some fluorocarbons, including a series of fluorocarbon liquid polymers. The study was made under a contract from the Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee, and we are indebted to them for the use of the compounds and for a compilation of certain physical properties. In addition to thirteen chlorotrifluoroethylene polymers, there were available four samples of fluorolube oil, three heavily fluorinated cyclohexane derivatives, and hexadecafluoroheptane. Values of density, index of refraction, molecular weight and viscosity were also furnished and are tabulated.

Experimental

The ultrasonic velocities in the above-mentioned compounds were measured over the temperature range 20 to 70°, using an ultrasonic interferometer[5] described earlier. It is of the conventional moving-reflector type, and satellites were removed by adjustment of the plane of the reflector. The ultrasonic frequency is obtained by applying the output of two separate high frequency oscillators to the grids of a mixer tube to produce a beat frequency of 500 kc./sec. in the tuned plate circuit of the mixer stage which drives the power amplifier. The plate circuit of the power amplifier is coupled to a resonant tank circuit by means of a variable link coupling.

The quartz crystal used to produce the ultrasonic wave in the liquid is X-cut and about 3.2 cm. in diameter. It is energized by the final tank circuit. As the interferometer reflector passes through successive half wave-length nodes, minima are indicated by the galvanometer in a vacuum tube voltmeter circuit.

The temperature of the liquids studied was controlled to ±0.03° by means of a water-bath in which the interferometer could be submerged. It was noted that the galvanometer dips were less sharp in the case of the compounds of high viscosity. In the case of Fluorolube oil of molecular weight 1233 (viscosity = 448.5 cs. at 60°) no nodes could be discerned and hence no velocities could be measured. The measured values of the ultrasonic velocity are listed in Tables I and II.

Results and Discussion

Low Velocity of Sound.—From Tables I and II and Fig. 1 it may be seen that the velocity at any one temperature increases with increase in the molecular weight of the compound for each of the series. A similar change has been observed for liquid silicone polymers.[4] On the other hand, Weissler, Fitzgerald and Resnick[3] noted a general decrease of velocity with increase in molecular weight for the ethylene glycol polymers.

Perhaps the most striking feature of the results is that, in very case, the substitution of fluorine for hydrogen in the molecule has resulted in a compound yielding an extraordinarily low value

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[1] This work was done under contract with Carbide and Carbon Chemicals Corporation.

[2] Now at Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee.

[3] Weissler, Fitzgerald and Resnick, *J. Applied Phys.*, **18**, 434 (1947).

[4] Weissler, New York meeting of the American Chemical Society, Sept. 16, 1947, reported on ultrasonic velocity in liquid silicone polymers.

[5] McMillan and Lagemann, *J. Acoust. Soc. Am.*, **19**, 956 (1947).