solutions of triethanolamine borate in water results in an immediate change of the indicator to its acid color, followed by slow neutralization and return of the solution to the basic side. The amount of acid required for complete neutralization approaches the stoichiometric value asymptotically. The rate of the reaction was determined from the half-time. In one determination, for example, 25 ml. water, one-half of a stoichiometric amount of hydrochloric acid, and 2 drops modified methyl orange were placed in a 250-ml. beaker. A capsule containing a standard solution of borate in acetonitrile was then smashed in the beaker, and the mixture was stirred. The time interval between the rupture of the capsule and the color change of the indicator was taken as the half-time of the reaction. In a series of such runs, the half-times were independent of the initial concentrations of reactants; the rate is independent of the acid concentration. Data are given in Table III.

TABLE III

RATES OF NEUTRALIZATION OF TRIETHANOLAMINE BORATE BY HYDROCHLORIC ACID AT 25° AND 0°

Initial concentrations of reactants, mole/l. Triethanolamine borate	Hydrochloric acid	Half-time at 25°, sec.	Rate constant, k_1, at 25° sec.$^{-1}$ × 10^3	Half-time at 0°, sec.	Rate constant, k_1, at 0° sec.$^{-1}$ × 10^4
0.0357	0.0179	181	3.83	1680	4.13
.0241	.0121	184	3.77	1624	4.27
.0182	.0091	187	3.71	..	..

In glacial acetic acid, perchloric acid gives similar results. Crystal violet was used as indicator. The half time for this reaction at 25° was also determined and found to be 220 sec., $k_1 = 3.15 \times 10^{-3}$ sec.$^{-1}$.

The neutralization of the amine in nitrobenzene by methanesulfonic acid proceeded much more slowly. The reaction did not exhibit simple kinetics and will be investigated further.

Rates and Activation Energies in the Menschutkin Reaction.—Acetonitrile was used as the solvent. Equal amounts of equimolar solutions of the reactants were mixed at 25°. Samples were pipetted into thin-walled glass capsules. The sealed capsules were placed in a constant temperature bath (±0.01°). At appropriate intervals a capsule was removed from the bath, broken under dilute sulfuric acid and titrated for iodide ion. The rate constants were calculated by utilizing the integrated rate expression for a second order reaction. Rate data for a typical determination are given in Table IV.

TABLE IV

RATE OF REACTION OF TRIETHANOLAMINE WITH METHYL IODIDE AT 40°[a]

Time, sec.	Ml. $AgNO_3$, x	Rate constant,[b] k_2 l./mole sec. × 10^4	Reaction, %
7200	1.54	4.39	13.1
14400	2.68	4.29	22.7
21600	3.59	4.27	30.5
28800	4.35	4.28	36.9
36000	4.89	4.15	41.5
40920	5.34	4.26	45.3
	$11.78 = a^1$	..	..

[a] Initial concentration of reactants at zero time, a, was 0.04756 M at 40°. Each capsule contained 5.08 ml. of solution (corrected for change in volume with increase in temperature). [b] Rate constants calculated from expression $k = \frac{1}{ta}\left(\frac{x}{a^1 - x}\right)$ where x and a^1 are expressed in ml. of silver nitrate solution.

The triethanolamine for rate determinations was purified by vacuum distillation, b.p. 204° at 12.5 mm., followed by recrystallization from acetone. The highest freezing point observed was 21.15°. It was found that triethanolamine which was purified merely by distillation did not give good second order constants. The material probably contained some secondary amine although the boiling point was essentially constant. The impurity was not identified.

The rates with triethanolamine borate were determined in the same general way. These rates were extremely slow, however, proceeding at 25° to the extent of only about 8% in one month. Thus, the precision of the individual points in these runs left much to be desired. Nevertheless, fairly consistent values could be obtained by the application of the least squares method to the data.

LAFAYETTE, IND. RECEIVED NOVEMBER 27, 1950

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

Concerted Displacement Reactions. VI. *m*- and *p*-Substituent Effects as Evidence for a Unity of Mechanism in Organic Halide Reactions[1]

BY C. GARDNER SWAIN AND WILLIAM P. LANGSDORF, JR.

The value of the Hammett reaction constant (ρ), which expresses the sign and magnitude of *m*- and *p*-substituent effects, is found to depend, in a predictable way, on four factors: the structure of the substituent, the structure of the halide, the structure of the electrophilic reagent, and the structure of the nucleophilic reagent. The solvent is relatively unimportant unless it functions in the role of either electrophilic or nucleophilic reagent. Tables are given which permit one to predict in what direction ρ will change with a given change in any of these four factors. The variation in ρ is evidence against sharply differentiated mechanistic categories, and indicates that one mechanism or interpretation is adequate for most reactions of organic halides.

The most successful quantitative correlation between the structure of chemical compounds and the rates of their reactions is the Hammett equation, which expresses the effect of *m*- and *p*-substituents in compounds containing a phenyl group.[2]

$$\log (k/k_0) = \rho\sigma$$

Here k and k_0 are corresponding rate constants with and without any substituent, ρ is a constant characteristic of the reaction and σ is a constant characteristic of the substituent.[3]

Although the reaction constant, ρ, has been tabulated for 41 different series of reactions, it is

---

[1] Supported in part by a du Pont grant in aid of fundamental research. Paper presented in part at the Conference on Organic Reaction Mechanisms, Gordon Research Conferences, A. A. A. S., Colby College, N. H., July 7, 1948. For previous papers in this series, see THIS JOURNAL, **70**, 1119, 2989 (1948); **71**, 965 (1949); **72**, 2794, 4578 (1950).

[2] (a) Hammett, THIS JOURNAL, **59**, 96 (1937); (b) "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

[3] By 1940 this equation served to correlate the rates of 1763 reactions. With the 332 of these which had been measured experimentally up to that time the median deviation between calculated and observed rates was only ±15%, in spite of the fact that the variation in rate on changing from a *p*-methoxy to a *p*-nitro substituent averaged thirty-fold and exceeded a thousand-fold in several series.

Table I

Effect of Structure on the Magnitude of *m*- and *p*-Substituent Effects

The higher the entry in any column, the greater will be the tendency toward a negative value of ρ, *i.e.*, toward acceleration by electron-supplying *m*- or *p*-substituents in the halide.

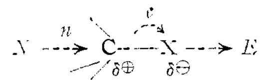
Structure of the substituent, σ	Structure of the halide, *S*	Structure of the electrophilic reagent, *E*	Structure of the nucleophilic reagent, *N*
p-CH_3O	$(C_6H_5)_3CX$	$AlCl_3$, Ag^+, Hg^{++}	C_6H_6
p-CH_3	$C_6H_5CH_2X$	H_2O, RCOOH, C_6H_5OH	RCOOH or C_6H_5OH
H	$C_6H_5CH_2CH_2X$	CH_3OH, $(CH_3)_2CO$, $CHCl_3$, RNO_2	H_2O or CH_3OH
p-Br	$C_6H_5COCH_2X$	C_6H_6	R_3N or RSH
p-NO_2	C_6H_5COX or $C_6H_5SO_3X$	Surface of glass wall or precipitated salts	HO^- or I^-

empirical, and little interpretation of its sign and magnitude has been offered for cases where the substituent is in an organic halide.[4]

This paper will attempt to demonstrate the factors which determine the sign and magnitude of ρ in polar (non-radical[5]) reactions of organic halides.

We shall purposely neglect the fact that there are intermediates of demonstrated stability in some of these reactions. Such intermediates can be detected by competition experiments,[6] spectral,[7] tracer[8] and other methods, and can often be characterized as either preceding or following the transition state by the presence or absence of "mass effects" of product ions,[6] by the difference in reactivity when different halogens are being displaced,[9] etc. It is likely that intermediates of at least some slight stability exist in *all* displacements, although our present techniques are often not sufficiently subtle to detect them. However, the over-all rates and reaction constants (ρ) depend not at all on the structure or energy of such intermediates but only on the ground state of the reactants and the transition state. Hence intermediates are irrelevant in the present discussion.[10]

When an ordinary polar displacement occurs, there are two essential covalency changes involved: *e*, the breaking of the old bond, and *n*, the making of the new bond. Neither process has begun in the reactants, both processes are complete in the products



but either process may have proceeded farther than the other at the transition state. The easiest route will not, in general, be one which results in the same fraction of completion of *e* and *n* at the transition state. Depending on whether *e* or *n* is more complete at the transition state when following this easiest route, the partial positive charge on the central carbon will be greater or less than in the ground state; and the difference in fractions of completion of *e* and *n* will determine the magnitude of this change in charge. *The reaction constant, ρ, is a measure of this change in charge*, and hence a criterion of the deviation from perfect synchronism involved, since the greater the increase in positive charge on this carbon at the transition state, the more electron supplying substituents will aid (the more negative will be ρ), and the greater the decrease in positive charge, the more electron withdrawing substituents will aid (the more positive will be ρ).

Experimentally, one finds a smooth, broad, continuous gradation of ρ values in the literature, all the way from highly negative values for Friedel–Crafts reactions of tertiary halides with benzene and aluminum chloride on the one hand to highly positive ones for reactions of aryl or benzoyl halides with hydroxide ion in water solution at the other extreme. There is no grouping of ρ values into categories that could correspond to different kinds of mechanisms (*cf.* last section of discussion). Inspection of the relative rate data reveals no duality or trinity of mechanism, but instead a continuous gradation of behavior over the entire range of cases usually considered, with ρ depending, in a predictable way, on four elements of structure: the structure of the substituent, the structure of the remainder of the halide, the structure of the electrophilic reagent (*E*), and the structure of the nucleophilic reagent (*N*), as shown in Table I. Both the electrophilic reagent and the nucleophilic reagent involved in the rate determining step must be considered. The solvent appears to be relatively unimportant in determining ρ except where it also functions in the role of either electrophilic or nucleophilic reagent or both.

These factors which affect the magnitude of ρ will be considered in order.

The Structure of the Substituent.—The Hammett equation assumes that the reaction and substituent constants are independent. However, one might expect ρ to be a function of σ for the following reason. A strongly electron-supplying substituent, *e.g.*, *p*-methoxy, should not only stabilize by resonance a transition state having a high positive charge on the R_3C group but, in so doing, it should also increase the *capacity* of the R_3C group (*including* substituent) *for positive charge*, and thereby favor more completion of bond break-

---

[4] Ref. 2b, p. 197.

[5] For factors determining the reaction constant in *free radical* reactions, see Swain, Stockmayer and Clarke, This Journal, **72**, 5426 (1950).

[6] Rate of reaction of *p,p'*-dimethylbenzhydryl chloride with various salts in aqueous acetone solution, Bateman, Hughes and Ingold, *J. Chem. Soc.*, 974 (1940).

[7] Transient yellow color with benzyl chloride and mercuric nitrate in aqueous dioxane solution, I. Roberts and Hammett, This Journal, **59**, 1063 (1937); ref. 2b, p. 140.

[8] Lack of dependence on *p*H of the ratio between rate of labeled carbonyl oxygen exchange and rate of hydrolysis of ethyl benzoate, indicating monoethyl orthobenzoate as an intermediate in both reactions; Bender, Abstracts of A. C. S. Meeting, Chicago, Ill., Sept. 5, 1950, p. 47N.

[9] Swain, Esteve and Jones, This Journal, **71**, 967 (1949).

[10] Of course, if a reaction is actually a succession of *two* displacements with different nucleophilic reagents involved in the two steps and with the first step rate determining, then the nucleophilic reagent involved in the first step is the one to consider in correlations of rate or reaction constant, even though it may not appear in the final product.

ing, relative to bond making, at the transition state (more negative ρ). A strongly electron-withdrawing substituent, *e.g.*, *p*-nitro, should increase the capacity of the R_3C group for negative charge, and favor bond making (more positive ρ than the mean). This would predict a positive curvature (concave up) on a plot of log k/k_0 *vs.* σ, and this is indeed what is found experimentally in many simple reactions.[11] Figures 1 and 2 give examples. Other examples are the reaction of piperidine with substituted chlorobenzenes, where the *p*-amino ($\sigma = -0.66$) and unsubstituted ($\sigma = 0.00$) compounds react at practically the same rate, but *p*-cyano ($\sigma = +0.52$) and *p*-nitro ($\sigma = +0.78$) enormously faster[13]; and the allylic rearrangement of substituted phenylpropenylcarbinols.[14]

If this curvature is due to resonance in the transition state, lower rates should be obtained with substituents which cannot interact effectively by resonance with the reacting center in the transition state. It might be expected that *m*-substituents as a class would fall into this category, because one cannot draw conventional resonance forms for interaction involving a *m*-substituent. This is borne out by the results with substituted benzyl chlorides and triethylamine in benzene solution (Fig. 1), by the reaction of benzyl bromides with pyridine in 90% ethanol (where *m*-nitro, the only *m*-substituent studied gave the lowest rate)[15] or in dry acetone (Fig. 2),[16] by the hydrolysis of benzyl chlorides in 50% ethanol[17] or 50% acetone,[18] by the reaction of benzyl chlorides with iodide ion,[18] by the reaction of benzyl fluorides with ethoxide ion,[19] and even by the reaction of β-phenylethyl chlorides with iodide ion.[20] In all these cases, there is a separation of the data into two curves, one for *m*-substituents (including the unsubstituted compound), and one for *p*-substituents.

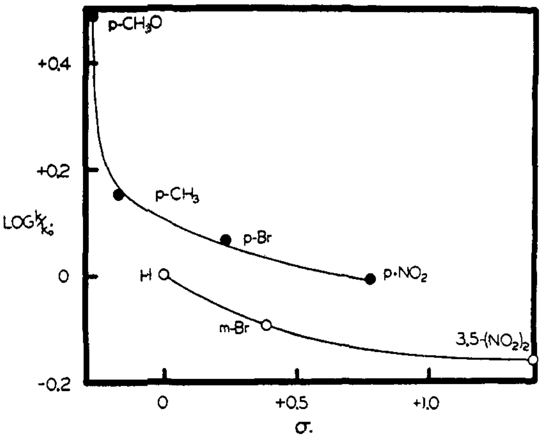


Fig. 1.—Benzyl chlorides with trimethylamine in benzene at 100°.

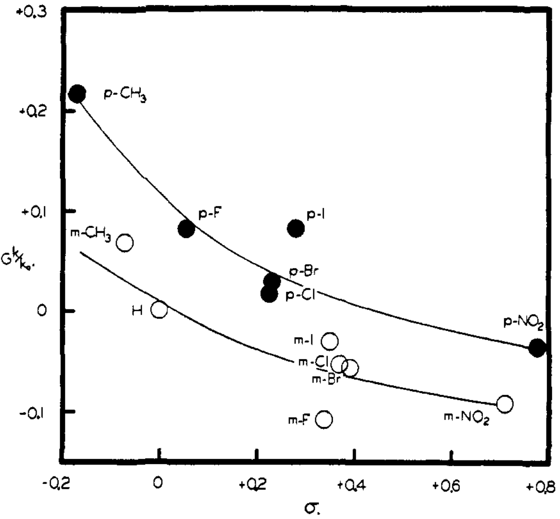


Fig. 2.— Benzyl bromides with pyridine in acetone at 20°.

Structure of the Halide.—With trityl and benzyl halides bond breaking tends to be more complete at the transition state than bond making (negative ρ). β-Phenylethyl halides are relatively unbiased. In the solvolysis of benzoyl halides bond making tends to be more complete (positive ρ). This is possible for displacements on either initially highly positive (*e.g.*, nitro, halogen, alkoxyl or acyl substituted) or, especially, unsaturated (carbonyl, aryl or vinyl) carbon atoms without violating the tetravalency of carbon. This case is common also for displacements on second row elements, (*e.g.*, silicon or sulfur atoms) which can expand their valence shells to give pentavalent intermediates.[9] The magnitude of the effect of structure can be seen by comparing the alcoholysis of triphenylmethyl chlorides ($k_{p\text{-CH}_3}/k_0 = 31$) with the alcoholysis of benzoyl chlorides (0.80). For other comparisons, see Table II. In the following discussion we will always compare values of $k_{p\text{-CH}_3}/k_0$ to be consistent. Except in one or two cases of especially serious curvature (see previous section), the same comparisons would hold using the $k_0/k_{p\text{-NO}_2}$ values.

The Structure of the Electrophilic Reagent.—The *more* electrophilic this reagent is, the greater will be the tendency for bond *breaking* to have proceeded to a greater extent than bond making at the transition state (more negative ρ). The order of electrophilicity is usually aluminum or mercuric halides > water, carboxylic acids or phenols > alcohols, acetone, chloroform, nitro compounds > benzene > glass wall or surface of salt crystals > saturated hydrocarbons. This order is fairly general since steric hindrance is seldom serious in the solvation of halogen, and the structure of the R_3C group makes itself felt only weakly and in-

---

(11) Previously, this curvature has often been ignored. *E.g.*, a straight line was fitted[2] to the data[12] on hydrolysis of benzoyl chlorides, giving $\rho = +0.796$. Actually there is a pronounced *minimum* at *p*-chlorobenzoyl chloride ($\sigma = +0.23$). By our interpretation, the bond making and bond breaking processes are truly synchronous for *p*-chlorobenzoyl chloride; with *p*-toluyl chloride ($\sigma = -0.17$), which reacts three times faster, bond breaking has proceeded somewhat farther than bond making at the transition state; but with *p*-nitrobenzoyl chloride ($\sigma = +0.78$), which reacts fourteen times faster, bond making has progressed much farther than bond breaking at this point.

(12) Berger and Olivier, *Rec. trav. chim.*, **46**, 516 (1927).

(13) Badger, Cook and Vidal, *J. Chem. Soc.*, 1109 (1947).

(14) Braude and Stern, *ibid.*, 1096 (1947).

(15) Baker, *ibid.*, 2631 (1932).

(16) Baker and Nathan, *ibid.*, 519, 1840 (1935); Baker, *Trans. Faraday Soc.*, **37**, 637 (1941).

(17) Olivier, *Rec. trav. chim.*, **41**, 646 (1922).

(18) Bennett and Jones, *J. Chem. Soc.*, 1815 (1935).

(19) Miller and Bernstein, THIS JOURNAL, **70**, 3600 (1948).

(20) Baddely and Bennett, *J. Chem. Soc.*, 1819 (1935).

TABLE II

TYPICAL CONCERTED DISPLACEMENT REACTIONS

Nucleophilic reagent (N)	Displaceable compound with *p*-substituent (Z) (S)	Electrophilic reagent (E)	Temp., °C.	Solvent	$k_{p\text{-}CH_3}/k_0$ [a]	$k_0/k_{p\text{-}NO_2}$ [a]	Ref.
C_6H_6	+ $ZC_6H_4SO_2Cl$	+ $AlCl_3$	30	C_6H_6	3.1	16[d]	*e*
CH_3OH	+ $(ZC_6H_4)_3CCl$	+ CH_3OH	25	C_6H_6	31[b]	....	*f*
C_2H_5OH	+ $ZC_6H_4C(C_6H_5)_2Cl$	+ C_2H_5OH	25	60% $(C_2H_5)_2O$–40% C_2H_5OH	4.1	92	*g*
H_2O	+ $ZC_6H_4CH_2Cl$	+ H_2O	70	50% $(CH_3)_2CO$–50% H_2O	13	13	*h*
H_2O	+ $ZC_6H_4CH_2Br$	+ Ag^+	30	90% C_2H_5OH–10% H_2O	45	55	*i*
H_2O	+ $ZC_6H_4CH_2Br$	+ H_2O	30	90% C_2H_5OH–10% H_2O	4.0	9	*i*
C_5H_5N	+ $ZC_6H_4CH_2Br$	+ H_2O	30	90% C_2H_5OH–10% H_2O	2.3	3.0	*j*
C_5H_5N	+ $ZC_6H_4CH_2Br$	+ H_2O	20	90% $(CH_3)_2CO$–10% H_2O	1.78	1.47	*j*
C_5H_5N	+ $ZC_6H_4CH_2Br$	+ $(CH_3)_2CO$	20	$(CH_3)_2CO$	1.64	1.09	*j*
C_5H_5N	+ $ZC_6H_4CH_2Br$	+ C_6H_6	100	C_6H_6	1.54	1.44	*k*
$(CH_3)_3N$	+ $ZC_6H_4CH_2Br$	+ C_6H_6	25	C_6H_6	1.41	1.21	*k*
$(CH_3)_3N$	+ $ZC_6H_4CH_2Cl$	+ C_6H_6	100	C_6H_6	1.55	1.02	*k*
C_5H_5N	+ $ZC_6H_4COCH_2Br$	+ $(CH_3)_2CO$	20	$(CH_3)_2CO$	0.94	0.42	*l*
H_2O	+ ZC_6H_4COCl	+ H_2O	0	50% $(CH_3)_2CO$–50% H_2O	2.4	.11	*m*
C_2H_5OH	+ ZC_6H_4COCl	+ C_2H_5OH	0	C_2H_5OH	0.80	.059	*n*
$C_6H_5NH_2$	+ ZC_6H_4COCl	+ C_6H_6	25	C_6H_6	.57	.12	*o*
$C_5H_{10}NH$	+ ZC_6H_4Cl	+ C_6H_6	80	C_6H_6	.94[c]	.066	*p*
I^-	+ $ZC_6H_4CH_2Cl$	+ $(CH_3)_2CO$	20	$(CH_3)_2CO$	....	.17	*h*
I^-	+ $ZC_6H_4CH_2CH_2Cl$	+ $(CH_3)_2CO$	75	$(CH_3)_2CO$	....	.15	*q*
HO^-	+ $ZC_6H_4COOC_2H_5$	+ H_2O	25	56% $(CH_3)_2CO$–44% H_2O	0.40	.012	*r*

[a] All rate ratios (R) have been adjusted to 25° by the expression (298) ($\log R_{25°}$) = (T) ($\log R_T$) where T is the absolute temperature of the experiment. This is a minor adjustment, and largely corrects for the differences in temperature of the various experiments, since the entropies of activation are very nearly constant for different *m*- and *p*-substituents. [b] Substituent (Z) was *p*-*t*-C_4H_9 rather than *p*-CH_3. [c] Substituent (Z) was *p*-NH_2 rather than *p*-CH_3. [d] Substituent (Z) was *m*-NO_2 rather than *p*-NO_2. [e] Olivier, *Rec. trav. chim.*, **33**, 244 (1914). [f] Swain, THIS JOURNAL, **70**, 1119 (1948). [g] Nixon and Branch, *ibid.*, **58**, 492 (1936). [h] Ref. 18. [i] Baker, *J. Chem. Soc.*, 987 (1934). [j] Ref. 16. [k] Date obtained in this investigation. [l] Baker, *J. Chem. Soc.*, 445 (1938). [m] Ref. 12. [n] Norris, Fasce and Staud, THIS JOURNAL, **57**, 1415 (1935); Norris and Young, *ibid.*, **57**, 1420 (1935). [o] Williams and Hinshelwood, *J. Chem. Soc.*, 1079 (1934). [p] Ref. 13. [q] Ref. 20. [r] Tommila and Hinshelwood, *J. Chem. Soc.*, 1801 (1938).

directly, through the halogen atom. The highest value of $k_{p\text{-}CH_3}/k_0$ in Table II is in the hydrolysis of benzyl bromides with silver nitrate as the electrophilic reagent; this is 45. With sufficiently strong electrophilic reagents for solvating the leaving group, bond breaking is favored ($k_{p\text{-}CH_3}/k_0$ greater than 1.0, ρ negative) even where the structure of the compound undergoing displacement is normally more favorable to bond making (*cf.* previous section) such as displacements on second row atoms which are electronically unsaturated and can expand their valence shells: *e.g.*, $k_{p\text{-}CH_3}/k_0$ for the reaction benzene + benzene sulfonyl chlorides + aluminum chloride is 3.1. As less electrophilic reagents for the leaving group are employed, the helpful effect of the *p*-methyl group steadily decreases. Thus, the value for the reaction of benzyl bromide with water in silver nitrate solution is 45; without silver it is 4.0. The value for the reaction with pyridine in 90% ethanol–10% water is 2.3; in 90% acetone–10% water it is 1.8; in dry acetone it is 1.64; in benzene solution it is 1.54.[21]

Structure of the Nucleophilic Reagent.—The *more* nucleophilic this reagent is, the greater will be the tendency of bond *making* to have proceeded to a greater extent than bond breaking at the transition state (smaller $k_{p\text{-}CH_3}/k_0$, more positive ρ). For example, the $k_{p\text{-}CH_3}/k_0$ ratio with benzyl bromide in aqueous ethanol is 4.0 with water but 2.3 with pyridine; and in benzene solution it is 1.54 with pyridine but 1.41 with trimethylamine. A particularly large effect results if two changes are made at once, to a more nucleophilic reagent and a less electrophilic reagent: the $k_{p\text{-}CH_3}/k_0$ ratio with benzyl chloride is 13 with water in aqueous acetone but 1.55 with trimethylamine in benzene solution; also this ratio for benzoyl chloride is 2.4 with water in aqueous acetone but 0.57 with aniline in benzene solution.

The order of nucleophilicity is usually benzene (in Friedel–Crafts alkylations) < carboxylic acids < water or alcohols < thiols or amines < iodide ion or hydroxide ion. This is far from an invariant order, however. Although a nucleophilic attack is always required, the nature of this "push" may vary from the early formation of a covalent bond by donation of an unshared electron pair (benzoyl halides) to a largely electrostatic interaction in the transition state (tertiary halides), depending on the structure of the halide. Steric hindrance is also a considerable factor. Thus, with respect to methyl bromide in benzene solution, pyridine is more nucleophilic (*i.e.*, reacts faster) than methanol by five powers of ten; but with respect to the sterically hindered trityl bromide, methanol is more nucleophilic than pyridine by six powers of ten. The slightly faster solvolysis in aqueous ethanol solution of methyl bromide than of ethyl bromide is probably also a steric effect.[22]

---

(21) Part of the observed decrease with less electrophilic solvents may be due to decreased association between the solvent and the nucleophilic reagent, which would increase the nucleophilicity of the latter and also produce a decrease (*cf.* next section).

(22) One might write $\rho = \tau\sigma + \rho_0 = \tau\sigma + S + E + N$ and $N = N_0 + \nu S - H$ where ρ_0 is independent of the substituent. τ is a measure of the difference between transition state and ground state resonance and dependent primarily on the structure of the R_3C group, S is charac-

Lack of Dependence on the Solvent.—*p*-Alkyl substituents increase the rate of alcoholysis of triphenylmethyl chloride in benzene solution enormously, at least as much as in more polar solvents such as 40% alcohol (*cf.* Table II). This indicates that the charge on carbon is at least as positive at the transition state in benzene solution as in the hydroxylic solvent, *i.e.*, that the "ionization" is not made less complete by the use of a less polar medium. This is evidently because in the benzene solution other reactants (hydroxylic solutes) have been provided for solvating carbon and for solvating halogen so that the solvent is not involved in either of these roles.[23]

Lack of Grouping into Mechanistic Categories.—Displacement reactions have been grouped into sharply differentiated mechanistic categories by Hughes, Ingold and co-workers. In the S_N1 mechanism only bond breaking has occurred at the transition state and no new bond having any covalent character at all has formed at this point[24]; the S_N2 mechanism is considered as a fundamentally different mechanism, with synchronous bond making and breaking[25]; unsaturated halides are segregated, because one can consider that with these only bond making has occurred at the transition state. Accordingly, one might expect ρ to be strongly negative, close to zero, and strongly positive for S_N1, S_N2, and unsaturated halide reactions, respectively. There is no suggestion of such a grouping experimentally. For example, the reactions of benzyl bromide in aqueous ethanol solution with water and pyridine, which were classified as S_N1 and S_N2, respectively,[26] have similar substituent effects ($k_{p\text{-CH}_3}/k_0$ ratios of 4.0 and 2.3, respectively). Yet hydrolysis of the same halide in the same medium but in the presence of silver ion gives a widely different effect (ratio of 45.) Baker and others have given more nebulous meanings to the terms S_N1 and S_N2 to avoid this difficulty,[27] but it is not clear that the distinction is worth retaining if it must be so blurred to fit the facts.

Previous papers of this series have shown that reactions of primary and tertiary halides need not differ in kinetic order. In this paper it has been shown that they do not differ qualitatively in the effect of substituents on the rate. There are no clear dividing lines to distinguish between "mechanisms" such as S_N1, S_N2, $B'2$, etc. There seem to be all degrees of intermediate behavior, and we have interpreted successfully the magnitude of the rate ratios (ρ) observed without using such "mechanisms." Thus once again it seems more appropriate, when discussing rates, to speak of a unity of mechanism and to use a single interpretation for most reactions of organic halides.

Experimental

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

Pyridine was Allied Chemical and Dye Co., redistilled, b.p. 115°; piperidine from Hooker Electrochemical Co., redistilled, b.p. 106–107°.

Trimethylamine was prepared by heating 25 ml. of 25% trimethylamine in aqueous solution with 25 g. sodium chloride under reflux. The escaping vapor was dried over potassium hydroxide pellets and finally Drierite and absorbed in 100 ml. of dry benzene in a gas washing bottle. The solution was stored over Drierite; concentration of the amine was determined immediately prior to use by titration with standard acid.

Benzyl chloride, b.p. 177.3–179.3°, benzyl bromide, b.p. 54.5–55° at 0.6–0.7 mm., *p*-nitrobenzyl chloride, m.p. 73.5–74°, and *p*-nitrobenzyl bromide, m.p. 98.2–99.2°, were Eastman Kodak Co. chemicals redistilled or recrystallized from benzene–petroleum ether.

p-Methoxybenzyl chloride was prepared by treating a solution of 12.6 g. (0.091 mole) *p*-methoxybenzyl alcohol[28] in 25 ml. of dry benzene with a solution of 10.9 g. of thionyl chloride in 25 ml. of dry benzene. The solution was heated under reflux on the steam-bath while the chloride was introduced into 1-2-ml. portions over a period of one-half hour. The solution was refluxed for an additional half-hour. The solvent was then removed and the residue vacuum distilled; 12.5 g. of a colorless liquid, b.p. 110–116° at 5–9 mm., was obtained. This was redistilled, and 12.4 g., 87% yield, of liquid, b.p. 92.5° at 1.5 mm., m.p. −1° was obtained.

p-Methylbenzyl chloride and bromide were made as follows. Trioxymethylene (42 g.) was added to the filtered Grignard reagent from 171 g. of Eastman Kodak Co. *p*-bromotoluene and 24 g. of magnesium turnings in 400 ml. of dry ether over a period of one hour with constant stirring. The mixture was stirred an additional 20 hours without added heat and was then decomposed with saturated ammonium chloride solution. The ether layer was washed with water, and the water layer extracted twice with ether. The combined ether extracts were evaporated on the steam-bath, and 81 g. of a light yellow oil which solidified upon cooling in an ice-bath was obtained. This solid was vacuum distilled, and the portion boiling at 105–108° at 4–5 mm. collected. The solidified distillate was recrystallized from ligroin with a b.p. 90–100°, yielding 32.5 g. (27%), m.p. 59.5–60°. Sixteen grams of Eastman Kodak Co. pure thionyl chloride dissolved in 25 ml. of dry benzene containing one drop of pyridine was treated with 15 g. of *p*-methylbenzyl alcohol dissolved in 25 ml. of dry benzene. The solution was refluxed for one hour, then washed once with ice-water and dried over calcium chloride. It was distilled through a Vigreux column and 11.8 g. (70% yield) of *p*-methylbenzyl chloride, b.p. 192°, was collected. Material prepared by an entirely different synthetic procedure[29] gave the same rate constant within experimental error. To make the bromide, anhydrous hydrogen bromide (Dow) was passed through a solution of 10 g. of *p*-methylbenzyl alcohol in 40 ml. of dry benzene for a period of 15 minutes. The solution was shaken by hand during the reaction and treated with 1 g. of Drierite when the first cloudiness appeared. It was then washed once with ice-water, dried over Drierite. Recrystallization from petroleum ether gave 11 g. (73% yield), m.p. 36–36.5°.

m-Bromobenzyl chloride was made *via* *m*-bromobenzyl

---

teristic of R_3CX, the compound undergoing displacement, E is the electrophilicity of the electrophilic reagent (defined as 1.00 for water), N_0 is the nucleophilicity (N) of the nucleophilic reagent toward an unhindered compound for which $S = 0$ (defined as 1.00 for water), ν is a measure of the difference between the covalent bonding ability and cation solvating ability of the nucleophilic reagent, and H measures the hindrance between the nucleophilic reagent and halide and depends on both. Work is being carried on in this Laboratory to separate these terms and assign quantitative magnitudes to each. For the effect of substituents, the expression $\rho = \tanh[\tau(\sigma - \sigma_0)] + \rho_0$ seems more justifiable than $\tau\sigma + \rho_0$, but the available data are not sufficiently accurate to warrant this many parameters.

[23] One or more molecules of solvent may be involved farther out in solvating the positively charged center, forming within the reagent attacking carbon, and this would affect the absolute magnitude of the rate. However, only one nucleophilic molecule and one electrophilic molecule appear to attack the molecule undergoing displacement *directly*, hence only these two reagents have a large effect on the ratio of rates, ρ.

[24] "Unimolecular reactions should never entail the covalent attachment, wholly or partly, of more than four groups to the reactive carbon atom" (Hughes, *Quarterly Reviews*, **2**, 125 (1948)). "There is no discernible steric effect in unimolecular substitution" (Dostrovsky, Hughes and Ingold, *J. Chem. Soc.*, 173 (1946)).

[25] Hughes, ref. 24; also *J. Chem. Soc.*, 968 (1946).

[26] Hughes, *Trans. Faraday Soc.*, **34**, 190 (1938).

[27] Baker, *J. Chem. Soc.*, 632 (1941).

[28] Davidson and Bogert, THIS JOURNAL, **57**, 905 (1935).

[29] Blanc, *Bull. soc. chim.*, **33**, 313 (1923).

alcohol. A solution of 13.2 g. (0.065 mole) of Eastman Kodak Co. *m*-bromobenzoic acid (recrystallized from alcohol, m.p. 154.2–154.7° (cor.)), in 150 ml. of dry ether was slowly added to 7 g. (0.0815 *active* mole) of lithium aluminum hydride dissolved in 200 ml. of dry ether over a period of 20 minutes. Since the mixture became pasty, an additional 100 ml. of ether was added. Stirring was continued for ten minutes and mixture was then decomposed with water, ice and 10% sulfuric acid. The layers were separated, the ether layer was washed with water, dried and the solvent removed by distillation. Upon vacuum distillation of the residue 11.15 g. of a colorless liquid, b.p. 120–122° at 2–3 mm. (92% yield) was obtained. A mixture of 11.15 g. (0.06 mole) of *m*-bromobenzyl alcohol, 50 ml. dry benzene, 2 drops pyridine, and 10.7 g. (0.09 mole) of thionyl chloride was refluxed for one-half hour. After removal of the solvent and excess chloride, the residue was vacuum distilled, and 10.3 g., 85% yield, of a liquid, b.p. 90–95° at 1.5 mm., was obtained. The liquid solidified to a slightly pink solid, m.p. 21.4–21.8°. Recrystallization from cold petroleum ether yielded white crystals, m.p. 22–22.1°.

p-Bromobenzyl chloride was similarly prepared *via* the alcohol. A yield of 9.1 g. (82%) of the alcohol, m.p. 76–77°, was obtained in this case. A solution of 9.1 g. (0.0486 mole) of *p*-bromobenzyl alcohol in 30 ml. of dry benzene containing two drops of pyridine was treated with 5.8 g., 0.0486 mole, of thionyl chloride in 25 ml. of dry benzene. After refluxing 30 minutes, the solvent was removed, and the residue was distilled, yielding 7.4 g. (75%) of white solid, b.p. 110° at 2 mm., m.p. 37–38°. Recrystallization from ether, benzene, chloroform and petroleum ether, successively, gave m.p. 37.5–38.0°. *p*-Bromobenzyl chloride was also prepared by the method of Dippy and Williams.[30] A white solid, 7.0 g., 7% yield, m.p. 49.8–50.6°, was obtained. It was shown that this compound was not pure *p*-bromobenzyl chloride by measuring its rate of reaction with trimethylamine. About half of the material reacted almost at once, a characteristic of the benzyl bromides. It appears, therefore, that the compound reported by these workers was actually a mixture of *p*-bromobenzyl bromide and *p*-bromobenzyl chloride. The other (first) sample was used in run no. 44.

3,5-Dinitrobenzyl chloride was prepared by treating a solution of 5.6 g. (0.0308 mole) of 3,5-dinitrotoluene[31,32,33] in 100 ml. of dry carbon tetrachloride with chlorine gas for fourteen hours with constant illumination from a 400 watt mercury arc lamp. Progress of the reaction was followed by the method of Barham and Thomson.[34] After the reaction had ceased, the chlorine flow was stopped, and 70 ml. of the solvent was removed by distillation. Upon refrigeration of this solution, 2.9 g. of light yellow solid was obtained, m.p. 73–74°. This solid was recrystallized from benzene–ligroin and twice from chloroform–petroleum ether, yielding 2.0 g. (31%) pale yellow crystals, m.p. 79.2–79.7°.

Anal. Calcd. for $C_7H_5O_4N_2Cl$: C, 38.82; H, 2.33; N, 12.94; Cl, 16.37. Found: C, 39.04; H, 2.35; N, 13.14; Cl, 16.18.

A sample of 3,5-dinitrobenzyl chloride, 0.3208 g., 0.00148 mole, was hydrolyzed in 50% water–50% acetone solution. After three weeks at 100°, 0.2432 g. (83% yield) of a light tan solid was obtained. After recrystallization from benzene–petroleum ether solution, the 3,5-dinitrobenzyl alcohol was light yellow, m.p. 89.5–90.5°.

Anal. Calcd. for $C_7H_6O_5N_2$: C, 42.43; H, 3.05. Found: C, 42.68; H, 3.40.

This product is the alcohol and not the phenol which would be obtained if the original chloride possessed a nuclear halogen; the product gave zero titer with sodium hydroxide under conditions which permitted titration of 2,4-dinitrophenol.

Reaction Products.—Substituted benzyl halides were allowed to react with various nucleophilic reagents in dry benzene solution under kinetic conditions and the products isolated and analyzed for halogen in a sufficient number of reactions to be certain that the product was known and was formed quantitatively.

For example, 10 ml. of a 0.1–0.4 *M* solution of each substituted benzyl chloride and 10 ml. of 0.5 *M* trimethylamine was allowed to react for at least one week at 100°. After filtering, washing with four 10-ml. portions of dry benzene, and drying for at least 1.5 hours at 61° and 0.15 mm., trimethylammonium salts were obtained with the following analyses and yields (of material with the analysis reported).

Substituent	Formula	Chlorine, % Calcd.	Chlorine, % Found	Yield, %
p-CH_3O	$C_{11}H_{12}ONCl$	16.44	16.27	98.6
p-CH_3	$C_{11}H_{12}NCl$	17.75	17.79	94.5
p-Br	$C_{10}H_{15}NBrCl$	13.40	13.44	91.0
m-Br	$C_{10}H_{15}NBrCl$	13.40	13.48	95.0
p-NO_2	$C_{10}H_{15}O_2N_2Cl$	15.37	15.39	95.0

The 3,5-dinitro compound was dried at 120° and analyzed also for carbon and hydrogen.

Anal. Calcd. for $C_{10}H_{14}O_4N_3Cl$: C, 43.56; H, 5.12; Cl, 12.86. Found: C, 43.59; H, 5.40; Cl, 12.75.

Kinetic Measurements.—The procedure has been described previously.[35] The water extracts were acidified with 5 ml. of 0.2 *M* nitric acid and titrated with 0.02898 *N* mercuric nitrate, after adding 4 drops of a saturated alcohol solution of *s*-diphenylcarbazide as an indicator. In a few cases (including only runs 19, 30, 31, 33 in Table II) the alternate method of quenching with excess hydrochloric acid and back titrating with standard sodium hydroxide, without extraction, was used.

Table III gives second order rate constants which we have determined from some typical runs. The average deviation of the rate constant from the mean was calculated for the

TABLE III

REACTION OF AMINES (N) WITH BENZYL HALIDES (S) IN BENZENE (E) SOLUTION

Run no.	N	S	$[N]$ (M)	$[C]$ (M)	Temp. (°C.)	k_2 (M^{-1} min.$^{-1}$)
14	C_5H_5N	$C_6H_5CH_2Cl$	0.199	0.205	100	0.0003
24	C_5H_5N	*p*-$CH_3C_6H_4CH_2Br$	.062	.050	100	.0589
32	C_5H_5N	$C_6H_5CH_2Br$	.123	.108	100	.0416
3	C_5H_5N	*p*-$NO_2C_6H_4CH_2Br$	.149	.077	100	.0311
39	$(CH_3)_3N$	*p*-$CH_3OC_6H_4CH_2Cl$	.058	.053	100	.167
28	$(CH_3)_3N$	*p*-$CH_3C_6H_4CH_2Cl$	.078	.057	100	.0773
12	$(CH_3)_3N$	$C_6H_5CH_2Cl$	.109	.079	100	.0544
44	$(CH_3)_3N$	*p*-$BrC_6H_4CH_2Cl$	.148	.083	100	.0631
40	$(CH_3)_3N$	*m*-$BrC_6H_4CH_2Cl$	.091	.071	100	.0435
13	$(CH_3)_3N$	*p*-$NO_2C_6H_4CH_2Cl$	.109	.088	100	.0534
38	$(CH_3)_3N$	3,5-$(NO_2)_2C_6H_3CH_2Cl$	.114	.067	100	.0377
31	$(CH_3)_3N$	*p*-$CH_3C_6H_4CH_2Br$	.048	.044	25	.611
30	$(CH_3)_3N$	$C_6H_5CH_2Br$	.051	.046	25	.432
33	$(CH_3)_3N$	*p*-$NO_2C_6H_4CH_2Br$	.054	.048	25	.356
17	Brucine	$C_6H_5CH_2Cl$	.061	.053	100	.126
19	$C_5H_{10}NH$	$C_6H_5CH_2Cl$	.306	.075	100	.076

TABLE IV

RUN NO. 44. REACTION OF 0.083 M *p*-BROMOBENZYL CHLORIDE WITH 0.148 M TRIMETHYLAMINE IN BENZENE AT 100°

Time (min.)	Ml. $Hg(NO_3)_2$ 0.02898 N	Ml. net titer after blank	Reaction, %	k_2 (M^{-1} min.$^{-1}$)
0	0.16	0.01	. .	. . . .
12	1.65	1.50	10.5	0.0636
28	3.28	3.13	21.9	.0634
47	4.88	4.73	33.1	.0644
77	6.80	6.65	46.5	.0642
104	7.92	7.77	54.4	.0621
126	8.84	8.69	60.8	.0633
150	9.54	9.39	65.6	.0622
183	10.42	10.27	71.8	.0630
335	12.49	12.34	86.4	.0614
20160	14.39	14.24	99.6	. . . .
			Average k_2	0.0631

---

(30) Dippy and Williams, *J. Chem. Soc.*, 164 (1934).

(31) "Organic Syntheses," Coll. Vol. I, p. 106.

(32) Brady, Day and Rolt, *J. Chem. Soc.*, **121**, 527 (1922).

(33) Cohen and McCandlish, *ibid.*, **87**, 127 (1905).

(34) Barham and Thomson, *Ind. Eng. Chem., Anal. Ed.*, **20**, 60 (1948).

(35) Swain and Eddy, This Journal, **70**, 2993 (1948).

points within each run; it was always less than 6% and averaged 3.6% for the runs in this Table. Check runs with different initial concentrations of reactants were generally done, and gave average rate constants averaging within 3.5% of the corresponding runs reported in Table III. The rate was always found to be first order with respect to the halide and first order with respect to the nucleophilic reagent. Table IV gives detailed data for one of these runs.

Acknowledgment.—The authors are indebted to Professors P. D. Bartlett, L. P. Hammett, J. D. Roberts and S. Winstein for many constructive criticisms and suggestions.

CAMBRIDGE, MASS. RECEIVED AUGUST 1, 1950

[CONTRIBUTION NO. 105 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Copolymerization. XVII. The Over-all Rate of Copolymerization of Styrene–Diethyl Fumarate[1]

BY CHEVES WALLING[2] AND ELIZABETH A. MCELHILL

The rates of polymerization and copolymerization of styrene and diethyl fumarate have been measured in the presence and absence of 2-azobis-isobutyronitrile as initiator at 60°. The ratio of the rate constant for bimolecular crossed termination to the geometric mean of the rate constants for bimolecular termination of the individual monomers is approximately 7.75. Attempts to calculate the rate of thermal cross initiation for this monomer pair has led to anomalous results, since diethyl fumarate apparently inhibits the thermal polymerization of styrene.

An equation describing the over-all rate of copolymerization for the case of chain termination by bimolecular interaction of radicals has been developed by Melville, Noble and Watson,[3] and by Walling,[4] and may be expressed in the form

$$\frac{-\mathrm{d}([\mathrm{M}_1] + [\mathrm{M}_2])}{\mathrm{d}t} = \frac{(r_1[\mathrm{M}_1]^2 + 2[\mathrm{M}_1][\mathrm{M}_2] + r_2[\mathrm{M}_2]^2)I^{1/2}}{(r_1^2[\mathrm{M}_1]^2 + 2\phi r_1 r_2[\mathrm{M}_1][\mathrm{M}_2]\delta_2/\delta_1 + r_2^2[\mathrm{M}_2]^2(\delta_2/\delta_1)^2)^{1/2}} \quad (1)$$

where M's are monomer concentrations, I the rate of chain initiation, r's the monomer reactivity ratios for the monomer pair involved, and δ's the ratio of the rate constant for chain propagation to the square of the rate constant for chain termination of the individual monomers. The quantity ϕ represents the ratio of the rate constant for bimolecular cross termination to the geometric mean of the rate constants for bimolecular termination of the two monomers alone. Since all quantities but I and ϕ can be obtained from rate studies on the single monomers and measurements of copolymer compositions, and since I can be fixed, for example, by selecting an efficient chain initiator with a constant rate of decomposition such as 2-azobis-isobutyronitrile, equation (1) provides the means of determining ϕ by the measurement of over-all copolymerization rates. By this means, ϕ has been determined for the systems styrene–methyl methacrylate[4,5] and styrene–methyl acrylate.[4] In addition, it has been possible to determine as well the rate constant for cross initiation in the styrene–methyl methacrylate system.[4]

Experimental

Polymerization Technique.—Styrene was commercial material vacuum distilled before use. Diethyl fumarate came from two samples of commercial material, one fractionally distilled *in vacuo* by Mr. V. G. Simpson and the other kindly supplied by Dr. D. C. Seymour, both of this Laboratory, and having the physical constants b.p. 97° (10 mm.), $n^{20}\mathrm{D}$ 1.4416. Polymerizations were carried out on 4- or 5-ml. samples in sealed, evacuated tubes and polymer yields determined by the usual technique of polymer isolation by multiple precipitation and solution from benzene–petroleum ether followed by vacuum sublimation of solvent from a benzene solution. In the case of the thermal polymerizations, particular care was taken to exclude light by wrapping the tubes in tin foil. The rate of decomposition of 2-azobis-isobutyronitrile in diethyl fumarate was obtained by measuring the rate of nitrogen evolution with a gas buret from a solution of 1.0046 g. (6.09 millimoles) of azo compound in 15.0 ml. of diethyl fumarate in a reaction flask gently shaken in a 60° thermostat. In order to eliminate any apparent induction period brought about by absorption of oxygen by the radicals produced, air was displaced from the system by nitrogen and nitrogen bubbled through the solution for a few minutes prior to the start of the reaction.

Results and Discussion

The use of equation (1) in the treatment of over-all rates of copolymerization requires a known (preferably constant) rate of chain initiation and chain termination by a bimolecular process. In order to determine the rate of decomposition of 2-azobis-isobutyronitrile in diethyl fumarate the rate of nitrogen evolution from a solution of 2-azobis-isobutyronitrile in diethyl fumarate at 60° was measured and, in Fig. 1, the logarithm of the amount of azo compound remaining is plotted against time. The experiment was interrupted after seven hours since the polymerization of the fumarate proceeded far enough to yield a highly viscous reaction mixture, and a calculated value for the final volume of nitrogen was employed. From the data in the figure, a rate constant of 9.4×10^{-6} can be calculated for the decomposition of 2-azobis-isobutyronitrile. The rate constant of decomposition of 2-azobis-isobutyronitrile in xylene at 60° is approximately 1×10^{-5} sec.$^{-1}$, and is almost independent of the solvent used.[5a,6] Since the radicals from this initiator approach 100% efficiency in starting polymer chains, in the cases of styrene, methyl methacrylate and vinyl acetate,[4]

---

(1) For the previous paper in the copolymerization series see K. W. Doak, D. L. Dineen, THIS JOURNAL, **73**, 1084 (1951).

(2) Lever Brothers Company, 164 Broadway, Cambridge 39, Massachusetts.

(3) H. W. Melville, B. Noble and W. F. Watson, *J. Polymer Sci.*, **2**, 229 (1947).

(4) Walling, THIS JOURNAL, **71**, 1930 (1949).

(5) H. W. Melville and L. Valentine, *Proc. Roy. Soc. (London)*, **A200**, 337 (1950).

(5a) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

(6) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949).