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Analysis of the Swain–Moseley–Bown Equation and Comparison of the Results with Nucleophilicities Derived from Halonium Ion Reactions

Paul E. Peterson,* D. Warren Vidrine, Francis J. Waller, P. M. Henrichs, Steve Magaha, and Bruce Stevens

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208, and the Department of Chemistry, St. Louis University, St. Louis, Missouri 63156. Received March 21, 1977

Abstract: In 1956 Swain, Moseley, and Bown correlated the rates of solvolysis of a variety of alkyl and acyl derivatives through the equation $\log k/k_0 = c_1 d_1 + c_2 d_2$. The equation has now been transformed to the form $\log k/k_0 = sN + mY$, where the solvent parameter Y is a measure of ionizing power and N appears to represent either nucleophilicity or electrophilicity. Compounds whose reactions are sensitive to electrophilicity exhibit negative sensitivity parameters, s. The reaction of pentamethyleneiodonium hexafluoroantimonate (1) with aqueous solutions of nucleophiles or pairs of nucleophiles generated a nucleophilicity scale encompassing both anionic and uncharged nucleophiles. The scale shows a linear correlation with that generated by reactions of methyl iodide. It is inferred that the charge type of both nucleophiles and substrates is unimportant for S_N2 reactions in H_2O.

Recently there have been some substantial advances in our understanding of the role of nucleophilicity in organic reactions. The work of Ritchie and co-workers has shown that various reactants, including particularly triarylmethyl cations, tropylium ions, and diazonium ions, obey the rate law[1]

$$\log k - \log k_0 = N^+ \qquad (1)$$

The difference in the logarithms of the rate constants for reactions of a substrate with a nucleophilic system (e.g., N_3^- in CH_3OH) and for reaction with a standard system (H_2O nucleophile in H_2O solvent) is a constant, N^+, which represents the difference in nucleophilicity of the two systems. Compounds with a high range of reactivity were shown to exhibit the same sensitivity to differences in nucleophilicity. Furthermore, the N^+ scale differs from the nucleophilicity scales generated from rates of S_N2 reactions. Recently the first step of the hydrolysis reactions of esters and related compounds has been shown to follow eq 1, provided certain assumptions hold for the other processes which govern the overall rate.[2] It is possible that the N^+ nucleophilicities represent an important component of S_N2 nucleophilicities, but considerable mystery surrounds the situation.

On another front, the nucleophilic component of the rates of solvolytic reactions of methyl, primary, and secondary substrates (e.g., isopropyl tosylate) have been identified and quantitatively characterized.[3,4] This work grew, in part, from the experimental observation in Schleyer's group[5] that 2-adamantyl derivatives do not respond to an increase in the nucleophilicity of the solvent in the way that isopropyl derivatives do. In our own group a comparable study grew from the observation[6] that the high reactivity of now isolable halonium ion salts made them suitable for determining the nucleophilicity of carboxylic acids in a constant solvent, SO_2.

Both Schleyer's group[3] and ours[4] proposed sets of compound and solvent parameters for equations of the type

$$\log k_A - \log k_B = sN_A^B + mY_A^B \qquad (2)$$

Here k_A and k_B are rate constants for reaction in solvents A and B, N_A^B is the change in solvent nucleophilicity, Y_A^B is the change in solvent ionizing power, and s (1 in Schleyer's paper) and n are sensitivity parameters characteristic of the compound. In still another treatment[3a] the solvent response of solvolytic rates is regarded as occupying a spectrum the extremes of which are represented by the reaction of methyl and adamantyl derivatives.

Curiously a successful treatment of solvolytic rates involving an equation comparable to eq 2 was used by Swain, Moseley, and Bown approximately 22 years ago,[7] but it has not been extended as new solvents and compounds were explored. The correlation of Swain, Moseley, and Bown also involves two solvent parameters, d_1 and d_2, and two compound parameters, c_1 and c_2.

$$\log k - \log k_0 = c_1 d_1 + c_2 d_2 \qquad (3)$$

The rate constant, k_0, refers to the reaction in the standard solvent, 80% ethanol, also chosen as the solvent of zero Y value in the Winstein–Grunwald–Jones equation,[8]

$$\log k - \log k_0 = mY \qquad (4)$$

As Streitwieser[9] and others have pointed out, the choice of parameters for *tert*-butyl chloride, $c_1 = 1$ and $d_1 = 1$, has made the Swain–Moseley–Bown parameters of "no theoretical significance". Various authors of textbooks recorded them,[10] but no meaningful interpretation ever was found. In 1972 we reported in preliminary form a resolution of this dilemma which

involved analyzing the parameters c_1, d_1, c_2. and d_2 in terms of the desired ones, s, N, M. and Y.[4] However, we gave only the formulas for the conversion in our preliminary communication. In the recent paper from Schleyer's group the compound parameters are again said to be "of little mechanistic significance."[3a]

In unpublished studies in our group,[11] halonium ions were found to be relatively unsatisfactory probes for the nucleophilicity of relatively basic molecules (alcohols, ethers) in SO_2, owing to a decline in reaction rate as the reaction proceeded. Hydrogen bonded aggregates of protonated species may account for some of the results. On the other hand, the products of reactions of recrystallized pentamethyleneiodonium hexafluoroantimonate[1] with anionic nucleophiles in water showed evidence of a response to the nucleophilicity of the anions.[12] In the present paper we have further explored the quantitative aspects of this reaction in competition studies involving pairs of nucleophiles. Although some questions remain regarding the precision and interpretation of our results, a logarithmic nucleophilicity scale has been constructed[12] which, with the

$$\text{(5)}$$
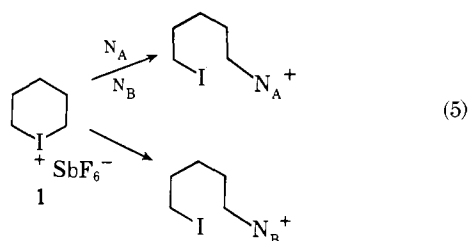
exception of the value for CN^-, parallels that generated by reactions of CH_3I in H_2O.

The sensitivity, s, in the Swain–Scott type equation, eq 6, is 0.77.

$$[\log k - \log k^{H_2O}]^{\text{halonium ion}} = s[\log k - \log k^{H_2O}]^{CH_3I} \quad (6)$$

In the present paper we extend our results[12] to include the nucleophilicity of some neutral molecules in water toward iodonium ion **1**. The analysis of the Swain–Moseley–Bown equation is described for the first time, and the resulting nucleophilicity scale is compared with our new one for neutral molecules in water solvent, and with the other recently derived scales.

The Swain–Moseley–Bown Equation

Transformation of the Equation. We begin by noting that eq 9–15 constitute a formal demonstration that the proportions of nucleophilicity and ionizing power in the solvent parameters[7] d_1 and d_2 is identical for all solvents. The solvent superscripts are then dropped from n_1, n_2, y_1, and y_2, eq 7 and 8. The reader who assumes this relationship (as we did initially) can proceed to the relatively direct analysis (eq 7 and 8, and eq 16–33).

We first assume that d_1 and d_2 are analyzable in terms of N and Y as follows:

$$d_1^S = n_1^S N_S + y_1^S Y_S \quad (7)$$

$$d_2^S = n_2^S N_S + y_2^S Y_S \quad (8)$$

Here N_S and Y_S are the solvent nucleophilicity and ionizing power, respectively. Initially, it is assumed that n_1 and n_2 (multipliers of N_S) and y_1 and y_2 (multipliers of Y_S) also are functions of the solvent, as indicated by the superscript S.[13]

For reaction of the compound RX

$$\log k_{RX}^S - \log k_{RX}^{80\% \text{ EtOH}} = c_1^{RX} n_1^S N_S + c_1^{RX} y_1^S Y_S + c_2^{RX} n_2^S N_S + c_2^{RX} y_2^S Y_S \quad (9)$$

$$\log k_{RX}^S - \log k_{RX}^{80\% \text{ EtOH}} = (c_1^{RX} n_1^S + c_2^{RX} n_2^S) N_S + (c_1^{RX} y_1^S + c_2^{RX} y_2) Y_S \quad (10)$$

We note by comparison with eq 2 that

$$s^{RX} = c_1^{RX} n_1^S + c_2^{RX} n_2^S \quad (11)$$

$$m^{RX} = c_1^{RX} y_1^S + c_2^{RX} y_2^S \quad (12)$$

For reaction in a second solvent S'

$$s^{RX} = c_1^{RX} n_1^{S'} + c_2^{RX} n_2^{S'} \quad (13)$$

$$m^{RX} = c_1^{RX} y_1^{S'} + c_2^{RX} y_2^{S'} \quad (14)$$

Equating expressions for s^{RX} and solving for c_1^{RX}/c_2^{RX}

$$c_1^{RX}/c_2^{RX} = (n_2^{S'} - n_2^S)/(n_1^S - n_1^{S'}) \quad (15)$$

Since c_1/c_2 ratios are not identical for various compounds[7] the right-hand side must be equal to $0/0$ (an indeterminant value). This result shows that n_2 values are not functions of solvent, but are identical for all solvents, as are the n_1 values. A corresponding proof shows the y_2 and y_1 values to be identical for all solvents.

We now establish additional relationships characterizing the n_1, n_2, y_1, and y_2 values based on the assigned[7] compound parameters for *tert*-butyl chloride, $c_1 = 1$ and $c_2 = 1$. For this compound, we also assign $s = 0$, and $m = 1$, approximately as suggested by Streitwieser.[9] Inserting these values in eq 13 and 14 yields

$$n_1 = -n_2 \equiv n \quad (16)$$

$$y_1 + y_2 = 1 \quad (17)$$

Equation 16 shows that the solvent parameters contain the nucleophilicity to extents equal in magnitude but opposite in sign, a consequence of the requirement that the sum $c_1 d_1 + c_2 d_2$ contain no nucleophilic component in the case of *tert*-butyl chloride. Equation 17 scales the y parameters to fit the Winstein–Grunwald–Jones equation, eq 4.

We may now evaluate y_1 and y_2 for two solvents, A and B, having the known or assumed ratio of nucleophilicities, N_A/N_B, as follows. The Swain–Moseley–Bown solvent parameters for solvent A may now be written

$$d_1^A = n N_A + y_1 Y_A \quad (18)$$

$$d_2^A = -n N_A = (1 - y_1) Y_A \quad (19)$$

Multiplying eq 19 by $y_1/(1 - y_1)$ and solving for $y_1 Y_A$ gives

$$y_1 Y_A = [d_2^A + n N_A][y_1/(1 - y_1)] \quad (20)$$

From eq 18

$$y_1 Y_A = d_1^A - n N_A \quad (21)$$

Equating the right sides of eq 20 and 21 gives

$$[d_2^A + n N_A][y_1/(1 - y_1)] = d_1^A - n N_A \quad (22)$$

Likewise for solvent B

$$[d_2^B + n N_B][y_1/(1 - y_1)] = d_1^B - n N_B \quad (23)$$

This equation can be multiplied by N_A/N_B to give, after rearranging terms,

$$(N_A/N_B) d_2^B [y_1/(1 - y_1)] - (N_A/N_B) d_1^B = -n N_A [y_1/(1 - y_1)] - n N_A \quad (24)$$

Also, from eq 22

$$d_2^A [y_1/(1 - y_1)] - d_1^A = -n N_A [y_1/(1 - y_1)] = n N_A \quad (25)$$

Equating the left sides of eq 24 and 25 and solving for $y_1/(1 - y_1)$ gives

$$y_1/(1 - y_1) = [(N_A/N_B) d_1^B - d_1^A]/[(N_A/N_B) d_2^B - d_2^A] \quad (26)$$

Table I. Comparison of $d_1 + d_2$ and Y Values

No. (Figure 1)	Solvent	$d_1 + d_2$	Y
1	97.5% Ac_2O	-3.43	-3.29
2	90% acetone–H_2O	-2.05	-1.86
3	AcOH	-1.70	-1.68
4	EtOH	-1.56	-2.03
5	MeOH	-0.78	-1.09
6	80% acetone–H_2O	-1.13	-0.67
7	70% acetone–H_2O	-0.84	0.13
8	80% EtOH–H_2O	0.00	0.00
9	50% acetone–H_2O	0.72	1.40
10	83% HCO_2H–H_2O	1.82	2.29
11	HCO_2H	2.13	2.05
12	H_2O	3.57	3.49

The right side yields a numerical value from which the numerical value of y_1 may be obtained. The key to the numerical evaluation of eq 26 was our measurement of the nucleophilicity ratio for acetic and formic acid reacting with tetramethylenehalonium ion. The ratio was very close to one in SO_2 solvent. (Our new results for H_2O solvent, reported in this paper, indicate that the ratio is approximately one in H_2O, also). Accordingly, we used $N_A/N_B = 1$, and with the reported d_1 and d_2 values, obtained the numerical values of eq 27 and 28.

$$y_1 = 0.10966 \qquad (27)$$

$$y_2 = 0.89034 \qquad (28)$$

There is a subtle trap in calculating y_1 values for the case where $N_A \neq N_B$. The N_A/N_B ratios, like Y_A/Y_B ratios, then depend on the choice of reference solvent (for which $N = 0$, $Y = 0$). In general, before our experimental values for the nucleophilicity of solvents can be used in eq 26, they must be scaled to an 80% ethanol reference. The fortunate occurrence of equal N values appears to have averted this problem. It is interesting that, based on the y_1 value given above, the d_1 parameters (cf. eq 18) accidentally represent relatively pure nucleophilicity parameters, nN, whereas formerly it was hypothesized[7] that values of $d_1 - d_2$ were a rough measure of nucleophilicity. We may solve eq 20 and 21 simultaneously to get these unscaled solvent nucleophilicities (n not assigned):

$$nN = d_1(1 - y_1) + d_2 y_1 \qquad (29)$$

$$nN = 0.89034 d_1 + 0.10966 d_2 \qquad (30)$$

It is especially interesting to note the simple relationship, obtained by addition of eq 18 to eq 19:

$$Y = d_1 + d_2 \qquad (31)$$

Finally, eq 11 and 12 for obtaining s and m values may be given in the forms

$$s/n = c_1 - c_2 \qquad (32)$$

$$m = (c_1 - c_2)y_1 + c_2 \qquad (33)$$

Since the y_1 values are small in absolute magnitude, based on the assumption of equal nucleophilicity of acetic and formic acid, c_2 is very close to m, as Streitwieser[9] has noticed. The simple relationship represented by eq 31 does not seem to have been noted previously.

Examination of the Converted Swain–Moseley–Bown Parameters. As we shall see, the Swain–Moseley–Bown reaction set is the only one examined to date in which a wide variation in the choice of substrate (both alkyl and acyl) and leaving group occurs. Accordingly an examination of the converted parameters yields insights not available from other sets.

In Table I the values of $d_1 + d_2$ (cf. eq 31) are given, along with the often used Y values based on tert-butyl chloride sol-
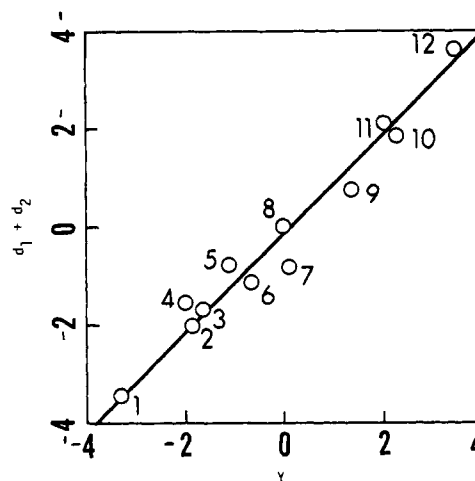
Figure 1. Plot of $d_1 + d_2$ vs. Y. Points are identified in Table I.

Table II. Converted Compound Parameters from Swain, Moseley, and Bown [a]

	s	m
MeBr	1.00	0.33
EtBr	0.83	0.41
i-PrBr	0.60	0.62
t-BuCl	0.0	1.00
EtOTs	0.77	0.29
i-PrOBs	0.28	0.50
2-Bromocyclohexyl OBs	-0.13	0.76
2-Methoxycyclohexyl OBs	0.0	0.57
$NO_2PhCOCl$	1.66	0.31
NO_2PhCOF	2.23	0.62
PhCOCl	0.55	0.55
PhCOF	1.32	0.74
$PhCH_2Cl$	0.57	0.47
$PhCH_2OTs$	0.57	0.42
$PhCHClCH_3$	-0.53	1.72
Ph_2CHCl	-0.02	1.25
Ph_2CHF	-1.60	1.25
Ph_3CSCN	-0.17	0.27
Ph_3COAc [b]	-0.24	0.66
$Ph_3COPhNO_2$	-0.77	0.55
Ph_3CF	-1.42	1.03
Ph_3CCl [c]	0.16	1.12

[a] Values from ref 7 except as indicated. [b] Values from ref 15. This revised value differs from that of ref 7. [c] Value from ref 16.

volysis. The plot of one set vs. the other (Figure 1) is impressively linear. This plot was shown in the original paper as a consequence of the assignment of the value 1 to the c parameters of tert-butyl chloride, giving the correlation equation log $k/k_0 = 1$ (d_1) + 1 (d_2). In retrospect it does not appear difficult to discern that the sum $d_1 + d_2$ should be free of nucleophilic components. However, the good fit of the plot vs. Y (Figure 1) is not a trivial result, since the d parameters are optimized to give a best fit with all of the compounds of the Swain–Moseley–Bown study.

We turn next to an examination of the compound parameters, since they are needed for our examination of the nature of the second solvent parameter, N. The scaling constant n in eq 30 and 32 is conveniently set equal to $1/0.53$ to make $s = 1$ for methyl bromide (eq 32) (cf. ref 7). The numerical forms of eq 32 and 33 are then

$$s = 0.53(c_1 - c_2) \qquad (34)$$

$$m = 0.10966(c_1 - c_2) + c_2 \qquad (35)$$

The resulting s and m values are listed in Table II. The compound parameters for methyl, ethyl, and isopropyl reactants reflect the now well-documented[3,4] roles of nucleophilicity and

ionizing power in the reactions of these substances. Perhaps the most noticeable feature among the remaining compounds is the occurrence of *negative s values*. These values reflect unusually rapid reactions in the least nucleophilic solvents used, acetic and formic acid, and they occur particularly for triphenylmethyl fluoride and diphenylmethyl fluoride. Electrophilic catalysis in the removal of the leaving group (cf. ref 14 and 15) nicely rationalizes the negative *s* values. Since among hydroxylic solvents the least nucleophilic are also the most acidic, it is not surprising that an apparent reversed sensitivity to nucleophilicity occurs. It will be interesting to see if a single solvent parameter, presently called N, is, in general, capable of reflecting both the nucleophilic and electrophilic components of reactions, as is the case for the very good correlations reported[7] by Swain, Moseley, and Bown. An exception would occur for a solvent which is both electrophilic and nucleophilic.

It should be noted that we owe our knowledge of acid catalysis of fluoride solvolyses primarily to research in Swain's group. In 1960 the rate of solvolysis of benzyl fluoride was shown[14] to be proportional to the Hammett acidity h_0. However, the anticipated observation of electrophilic catalysis in a restudy of the solvolysis of triphenylmethyl acetate[15] was clouded by the difficulty of understanding the nature of d_1 and d_2 parameters. These difficulties led Swain and co-workers[16] to invoke nucleophilic components in tertiary halide solvolyses, including that of *tert*-butyl chloride,[16] whereas our revised interpretation, Table II, shows normal sensitivities (*s* and *m* values) for chlorides. A possible exception is PhCHClCH$_3$, whose high *m* value and negative *s* value may reflect the difficulty of accommodating the phenomenon of "dispersion" in S_N1 reactions in solvents of comparable nucleophilicity.[9]

We note that zero *s* values would be expected to occur for compounds having balanced nucleophilic and electrophilic accelerations, with *tert*-butyl chloride the arbitrary zero point for electrophilic acceleration. This expectation is another consequence of encompassing a variety of leaving groups in a single correlation. Only those schemes, e.g., those of Peterson et al.[4] and Schleyer et al.,[3] which are confined to a single leaving group reflect a true sensitivity to nucleophilicity.

We further note that compounds whose reactions are less sensitive to electrophilicity than *tert*-butyl chloride are expected to show positive *s* values which actually reflect interactions in the *tert*-butyl chloride reactions. The high *s* values for the reactions of p-NO$_2$C$_6$H$_4$COF, p-NO$_2$C$_6$H$_4$COCl, and PhCOF are possible candidates. Less electrophilic catalysis than in the reaction of *tert*-butyl chloride might occur if the halide does not leave in the rate-determining step and if H bonding to the developing O$^-$ group is relatively unimportant. The very slow reaction of p-NO$_2$C$_6$H$_4$COF in CH$_3$CO$_2$H and HCO$_2$H is in accord with this suggestion, since loss of fluoride would be expected to be subject to electrophilic catalysis in these solvents, by analogy with the reaction of benzyl fluoride, mentioned earlier. In terms of eq 36 those acyl reactions with high *s* values would be postulated to exhibit rate-determining formation of the tetrahedral intermediate, which occurs when Y is such a good leaving group that no appreciable return to reactant (at rate k_{-X}) occurs. Accordingly it may seem puzzling that PhCOCl should show a lower *s* value, since Cl$^-$ is expected to be a better leaving group than F$^-$. We shall discuss this point later.

In general, the question of the relative magnitudes of k_X, k_{-X}, and k_{-Y} for various acyl derivatives reacting according to eq 36 appears to have remained a subject of controversy,
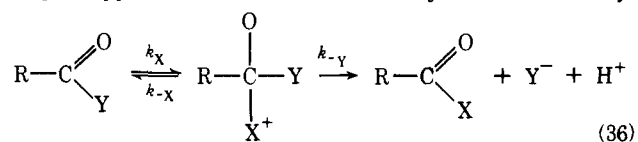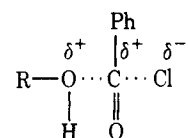
despite extensive study. Ritchie has recently proposed[2] an extraordinary unifying scheme for a range of reactions of acyl derivatives (cf. eq 36). The dependence of rate upon nucleophile follows N^+ when k_{-Y} is sufficiently fast. In these cases nucleophilic addition to the carbonyl group is rate determining. In other cases eq 37 is followed.

$$\log k_{\mathrm{obsd}} = \log k_0 - N^+ - \log[1 + k_{-X}/k_{-Y}] \quad (37)$$

It is interesting to examine the relationship of deductions based on *s* and *n* values with expectations derived from the Ritchie tabulation of k_{-X} and k_{-Y} values. We infer that the high *s* values for reaction of acyl fluorides, RCOF, reflect not only a tendency for F$^-$ to avoid bond breaking in the rate-determining step (as mentioned above) but also a full response to solvent nucleophilicity. According to Ritchie, this would be a nucleophilicity represented by the N^+ scale.

The results of Table II imply that electron-attracting groups in the acid moiety (e.g., in NO$_2$PhCOF and NO$_2$PhCOCl) favor a mechanism of the type shown in eq 36 in which the halogen does not leave in the rate-determining step. In terms of the Ritchie study it is not evident that substituents in the acyl moiety should affect the mechanism since it is the good leaving group ability of Y$^-$ relative to X$^-$ which gives this result. Fluorine ion has one of the largest k_{-Y} values among groups considered by Ritchie. Accordingly, for nucleophiles considered in his paper (but perhaps not for the nucleophile RCO$_2$H), the loss of Y$^-$ (eq 36) would be expected to be fast relative to X$^-$, and not rate determining for acyl fluoride reactions, as also postulated here. Chloride would presumably have a still larger value of k_Y. The response of PhCOCl to nucleophilicity is drastically reduced, however. The *s* and *m* values are comparable to those of isopropyl bromide, suggesting that a change in mechanism has occurred. The data suggest that a tetrahedral intermediate is no longer formed, but that instead a transition state, shown below, in the middle of the S_N1–S_N2

$$
\begin{array}{c}
\mathrm{Ph} \\
\overset{\delta^+}{}\;\overset{\delta^+}{|}\;\overset{\delta^-}{} \\
\mathrm{R-O\cdots C\cdots Cl} \\
|\quad \| \\
\mathrm{H}\quad \mathrm{O}
\end{array}
$$

spectrum occurs. The above-mentioned effect of electronegative substituents is accordingly the prevention of an S_N1-like reaction. Those acyl reactions in which tetrahedral intermediates are formed, but in which k_{-Y} may be rate determining (e.g., reactions of esters), do not appear to be represented in the Swain–Moseley–Bown tabulation.

The interpretations given above are essentially those which have been given previously, based on the effect of solvent ionizing power and other considerations.[17] The present investigation shows that correlation with both N and Y adds an apparently meaningful second dimension to the interpretation of solvent effects in acyl reactions. For some reactions of acyl derivatives in water, Jencks and co-workers[18a,b] and others[18c] have postulated that the rates of proton transfers in tetrahedral intermediates may be rate determining. For the wide range of solvents which we have treated above, it is not possible to evaluate such intricacies of mechanism. As in the early stages of any mechanistic study, the broad hypotheses which we have outlined represent a conceptual framework which may be expanded and replaced as data become available.

Halonium Ions as Probes of Nucleophilicity

Water. In our earlier experiments,[12] the reaction of iodonium salt **1** with water itself gave predominantly the ether **2** (eq 38). In more recent work the volume of water (or water containing a nucleophile) was increased from 2–5 mL to 100 mL, rapid magnetic stirring was employed, and the halonium ion was added in one portion instead of several portions. Under the
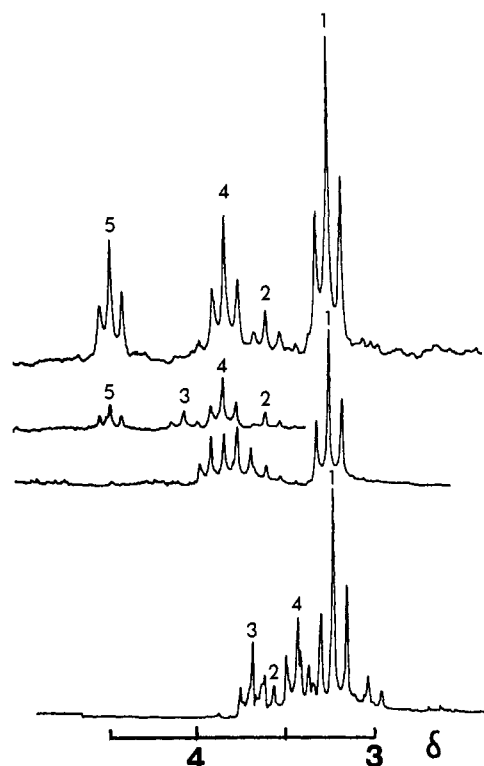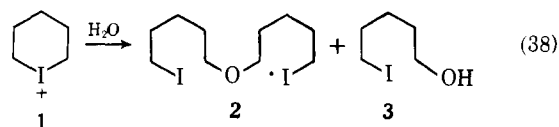
$$
\mathrm{R-C}\!\!\overset{\displaystyle O}{\underset{\displaystyle Y}{\Big\langle}} \;\underset{k_{-x}}{\overset{k_x}{\rightleftharpoons}}\; \mathrm{R-\underset{\underset{X^+}{|}}{\overset{\overset{O}{\|}}{C}}-Y} \;\overset{k_{-Y}}{\longrightarrow}\; \mathrm{R-C}\!\!\overset{\displaystyle O}{\underset{\displaystyle X}{\Big\langle}} + Y^- + H^+ \qquad (36)
$$

Figure 2. NMR analysis of the products of reaction of pentamethyleneiodonium ion with Cl^- and OH^-. A, $CDCl_3$ extract. B, extract with CF_3CO_2H added. C, trace of strong acid added, spectrum recorded immediately. D, spectrum recorded after complete trifluoroacetylation. Identification of triplets: 1, CH_2I; 2, CH_2Cl; 3, CH_2OH; 4, CH_2OR of ether 2; 5, $CH_2O_2CCF_3$.

Table III. Reactivities (25 °C) of Anionic Nucleophiles toward Pentamethyleneiodonium Ion (1)

Nucleophile[a]	Rel reactivities (competitors)[a]
H_2O	1
F^-	4.3 (H_2O)[b]
Cl^-	253 (H_2O)[b]
OAc^-	79 (H_2O)[b]
OH^-	1020 (Br^-)[c] 761 (SCN^-)[d]
	410 (I^-)[e] 583 (Cl^-)[f]
Br^-	1540 (Cl^-)[g]
SCN^-	10 200 (I^-);[h] 12 300 (Br^-)[i]
	11 900 (Cl^-)[j]
I^-	12 800 (Br^-)[k] 13 000 (Cl^-)[l]
CN^-	669[m] (Br^-)

[a] Anions present as sodium salts. [b] The area, CH_2F, CH_2Cl, or CH_2OAc (^{1}H NMR) was divided by the area for CH_2O and the result was multiplied by 55.3 to obtain the reactivity relative to 1 M H_2O. [c] Br^-/OH^-, 1.52. [d] SCN^-/OH^-, 15.1. (The value 761 is based on the average of the three values for SCN^- with halide competitors.) [e] I^-/OH^-, 31.3. [f] OH^-/Cl^-, 2.31. [g] Br^-/Cl^-, 6.12. [h] I^-/SCN^-, 1.25. [i] Based on the average of five values, SCN^-/Br^-, 7.94. The individual values were determined for 1 M NaBr and molarities of SCN^- as followed: 1, $^1/_4$, $^1/_8$, $^1/_{16}$, $^1/_{64}$. The respective reactivities, adjusted to 1 M NaSCN, were SCN^-/Br^- = 8.56, 8.60, 7.37, 6.62, 9.41. [j] SCN^-/Cl^-, 47.0. [k] I^-/Br^-, 8.3. [l] I^-/Cl^-, 51.3. [m] Br^-/CN^-, 2.31.

latter conditions alcohol **3** was the sole product observed. However, in reactions involving OH^- or CN^-, both **2** and **3**

$$\underset{\underset{\textbf{1}}{I^+}}{\bigcirc} \xrightarrow{H_2O} \underset{\textbf{2}}{\bigcirc_I \bigcirc_O \bigcirc_I} + \underset{\textbf{3}}{\bigcirc_I \bigcirc_{OH}} \qquad (38)$$

were observable by ^{1}H NMR at 90 MHz either before or after esterification with CF_3CO_2H containing a drop of strong acid (Figure 2). These results indicate that in the earlier experiments contact of the halonium salt with undissolved alcohol **3** accounted for the formation of **2** in water. In the latest experiments, reported here, this type of complication appears to be avoided.

For the competition experiments to be described, a key question is whether the reaction of iodonium ion with water is sufficiently slow to prevent complications arising from incomplete mixing. We have now performed a filtration experiment which indicates that ion **1** survives for a brief time in water solution. Addition of **1** to stirred H_2O at 0 °C followed by immediate filtration through a medium porosity fritted glass funnel into aqueous NaSCN gave a substantial amount of 5-iodopentyl thiocyanate (eq 5), whereas an experiment at room temperature with a 10-s delay prior to filtration gave little, if any, thiocyanate (NMR analysis). Unless solid ion passed through the filter in the experiment at 0 °C but not that at 25 °C, it may be inferred that ion **1** has an observable half-life in H_2O at 25 °C, perhaps roughly 1 s. This result is favorable for achieving competition reactions not influenced by mixing effects, although such effects cannot be rigorously ruled out for reactive nucleophiles.

Anionic Nucleophiles. The relative reactivities of anionic nucleophiles were determined from the ratios of reaction products formed in competition experiments between pairs of

nucleophiles. A possible additional test for the presence of mixing effects or other complications (micelle formation, reactions at the surface of the solid) is the response of product ratios to concentration changes. For the highly reactive pair Br^- and SCN^-, the relative reactivities, corrected for concentration, remain satisfactorily constant over a 64-fold range (Table III). The constancy of the values also indicates that the reproducibility of our rather unsophisticated analytical method is satisfactory for our purpose. It is noteworthy that if the competing reactions show the same response to ionic strength, the effect of the variable ionic strength cancels in these experiments.

The success of experiments at unequal concentrations suggested that a scale of nucleophilicity could be constructed using only a few pairs of nucleophiles of rather widely varying reactivity to span the range. The halide ions, Cl^-, Br^-, and I^-, were selected as these reference nucleophiles, along with H_2O. (F^- was too unreactive, compared to H_2O, to serve as an accurate reference.) The relative reactivities, based on ^{1}H NMR analysis of extracts, were as follows: Cl^-/H_2O (1 M) = 250; Cl^-/Br^- = 6.1; Br^-/I^- = 8.3. They represent a range of approximately 13 000-fold from H_2O to I^-. Among the five nucleophiles I^-, SCN^-, Br^-, OH^-, and Cl^-, ten reactivity ratios may be determined. These values, converted to reactivities relative to H_2O, are given in Table III, along with values for F^-, OAc^-, and CN^-. Among those values which serve as cross-checks the three which do not involve 5-iodo-1-pentanol as a reaction product show good internal consistency. Values derived from OH^-, based in part on the amount of 5-iodo-1-pentanol, show more variation. Possible inaccuracies associated with the properties of iodopentanol are mentioned in the Experimental Section.

Although only a range of values can be quoted for OH^-, the values in Table III, converted to a logarithmic nucleophilicity scale (Table IV), give an approximately linear plot (Figure 3) vs. log k_2 values from the literature[19] for the reactions of CH_3I with nucleophiles in H_2O. An exception is CN^-.

Several features of the halonium ion competition method for the determination of nucleophilicity are worthy of comment. The method is quite rapid. The products from the addition of approximately 0.3 g of halonium salt to 100 mL of aqueous nucleophile were extracted after only 60 s following

Table IV. Comparison of Scales of Nucleophilicity

Nucleophile	$[\log k/k_{H_2O}]^{H_2O}$ (for halonium ion 1)[a]	Nucleophilicity SS value (anions)[b] or SMB value (neutrals)[c]	CH$_3$I scale (anions)[d] or SBS scale (neutrals)[e]
I$^-$	4.11	5.0	5.41
SCN$^-$	4.06	4.8	5.42
Br$^-$	3.19	3.9	4.48
OH$^-$	2.8	4.2	4.69
Cl$^-$	2.40	3.0	3.36
OAc$^-$	1.90	2.7	
F$^-$	0.63		1.71
H$_2$O	0.00	0.00	0.00
MeOH	0.57^f	0.46	0.27
EtOH	0.50^g	0.25	0.35
i-PrOH	0.33		0.25
t-BuOH	−0.41		
(CH$_2$OH)$_2$	+0.33^h		
HCO$_2$H	0.37^i	−2.42	−1.79
CH$_3$CO$_2$H	−0.06^j	−2.42	−1.79

^{a} This work. Competitor nucleophiles for anions are listed in Table III. For neutrals, H$_2$O is the competitor. ^{b} Values of Swain and Scott, ref 21. ^{c} Values of Swain, Moseley, and Bown, ref 7. ^{d} Values in H$_2$O, ref 19. ^{e} Values of Schadt, Bentley, and Schleyer, ref 3a. ^{f} For 1 M MeOH. ^{g} Value for 2 M EtOH, 3.9 mol %. Other values observed were EtOH (50 wt %, 28 mol %, 9.9 M), $N = 0.59$; EtOH, 80 wt %, 61 mol %, 14.7 M, $N = 0.53$. ^{h} For 2 M (CH$_2$OH)$_2$; nucleophilicity calculated for 4 N ROH. ^{i} For 2 M HCO$_2$H and 1 M HClO$_4$, NMR analysis based on HC=O, δ 8.04, and CH$_2$O, δ 4.19. ^{j} For 1 M HOAc and 0.01 M HClO$_4$, NMR analysis. For 8.8 M HOAc and 1 M HClO$_4$, $N = 0.05$, NMR analysis. For 1 M HOAc and 1 M HClO$_4$, $N = -0.19$, gas chromatographic analysis by comparison with solution of distilled ester.

the addition. Accordingly, nucleophiles (e.g., HCO$_2^-$) whose products are subject to hydrolysis may be examined. Moderately weak nucleophiles were amenable to study (F$^-$, CH$_3$CO$_2$H) since their reaction products were determinable by 90-MHz ^{1}H NMR (F$^-$) or gas chromatography (CH$_3$CO$_2$H) in the presence of large amounts of the products of reaction with H$_2$O.

It is to be noted that the product of general base catalysis is counted as a product of reaction with water. For example, in our reaction of fluoride ion general base catalysis would occur according to the equation

$$F^- \cdots HOH + RI^+R \rightarrow HF + ROH + RI$$
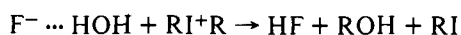
Unless the amount of ROH is comparable to the amount formed from the H$_2$O competitor, it will not greatly decrease the RF/ROH ratio upon which the values of Table IV are based. When the rate of disappearance of the reactant is used as a measure of nucleophilicity, general base catalysis artificially raises the apparent nucleophilicity (cf. ref 2). Among the nucleophiles of Table IV, the values for OAc$^-$ and F$^-$ may reflect the presence of some "water product" formed by general base catalysis.

The iodonium ion reactions whose products yielded the reactivity scale of Table IV were carried out at 1 M concentrations of at least one nucleophile for convenience in maintaining pseudo-first-order conditions. In studies involving the water-soluble substrate 1-methyl-3-(methyl sulfonate)pyridinium perchlorate,[20] S$_N$2 reactions were said to be approximately 1.4 times faster in solutions 0.1 M in nucleophile than in solutions which were 0.5 M. We have not applied a correction for concentration to the values (Tables III and IV) from our relatively unsophisticated study. Because of the previously mentioned approximate cancellation for ionic nucleophiles, only those reactivities measured relative to that of H$_2$O (Cl$^-$, F$^-$, OAc$^-$)
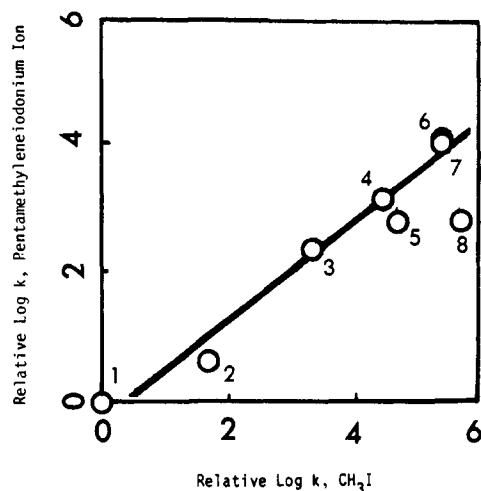

Figure 3. Plot of $\log k/\log k^{H_2O}$ for tetramethyleneiodonium ion vs. the values for CH$_3$I. Nucleophile: 1, H$_2$O; 2, F$^-$; 3, Cl$^-$; 4, Br$^-$; 5, OH$^-$; 6, I$^-$; 7, SCN$^-$; 8, CN$^-$. Slope = 0.77, CN$^-$ excluded from correlation.

are expected to be subject to substantial concentration effects.

The most familiar scale of anionic nucleophilicity is probably that of Swain and Scott[21] (cf. eq 40) also given, in part, in Table IV. Although the values are scaled to a CH$_3$Br standard, most of them were obtained from secondary sources, including reactions of epoxides and, in part, from reactions in mixed solvents. In comparison of our values with those of Swain and Scott, division of our values by 0.77 followed by division by 1.12 would be appropriate. The first operation converts to a CH$_3$I scale, using the iodonium/CH$_3$I slope of Figure 3. The second converts from the CH$_3$I scale to a CH$_3$Br scale.[19b]

From a synthetic standpoint it is to be noted that Br$^-$ and I$^-$ gave quantitative yields (>99%) of 1-bromo-5-iodopentane and 1,5-diiodopentane (cf. eq 1), as was verified by gas chromatographic comparison with standard solutions of these products. The possibility of synthesizing mixed dihalides which are otherwise not readily accessible was explored using 1-methyltetramethylenebromonium ion (4). Reaction of 16.8 g of the SbF$_6^-$ salt with concentrated HCl in H$_2$O gave the product 5 containing some 6 (8:1 ratio). The combined yield

(39)
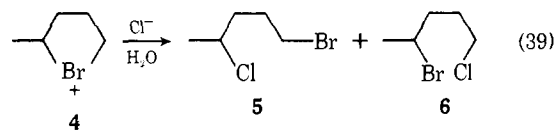
of distilled dihalides was 67%. It is interesting that, although the secondary bromonium ion bond is the better leaving group, indicating that the reaction has S$_N$1 character, the selectivity for Cl$^-$ in the presence of H$_2$O is maintained (cf. later discussion of the reaction of secondary substrates).

Uncharged Nucleophiles. Our study now encompasses the uncharged, oxygen-containing nucleophiles, CH$_3$OH, CH$_3$CH$_2$OH, (CH$_3$)$_2$CHOH, (CH$_3$)$_3$COH, HCO$_2$H, and CH$_3$CO$_2$H (cf. Table III). Whereas the Schleyer[3] and Peterson-Waller[4] approaches yield nucleophilicities in a solvent composed of the nucleophile itself, the present method gives the nucleophilicity in a *constant* solvent (H$_2$O in the instance reported here).

Presently it is known that there are large solvent effects upon the relative nucleophilicity of anions, particularly in alcohol or aqueous solvents compared to aprotic solvents.[22] Not surprisingly, the new data for uncharged species show some substantial effects attributable to the solvent. Formic and acetic acid in water are approximately *as nucleophilic as water itself*, whereas they are 1.8–2.4 log units less nucleophilic in the pure

Table V. Sensitivities to Nucleophilicity

Compd	s, Swain–Scott[a]	s, Swain–Moseley-Bown[b]	s, Peterson–Waller[c]	l, Schadt, Bentley, Schleyer[d]
CH_3Br	1.00	1.00		
EtBr		0.83	0.9	1.00
EtOTs	0.66	0.77	0.75	0.89
$PhCH_2Cl$	0.87	0.57		0.75
PhCOCl	1.43	0.55		
i-PrOTs		0.5	0.58	0.49-0.38
2-BuOTs			0.39	0.41-0.32

[a] Reference 21. [b] Reference 7. [c] Reference 4. [d] Reference 3a.

Table VI. Product Ratios and s Values for Reactions of Sulfonates in H_2O Containing OAc^- (Reference 28)

Substrate	Obsd ROAc/ROH	Assumed s	Calcd ROAc/ROH	Needed s
Methyl	5.4	0.9	4.9	0.92
Ethyl	1.9	0.8	2.6	0.75
2-Hexyl	0.11	0.4	0.22	0.29

solvents, as judged by Schleyer[3] and Swain–Moseley-Bown[7] scales. The Swain–Moseley-Bown N values may, however, have exaggerated magnitudes to accommodate the electrophilic solvent properties of carboxylic acids which these values also reflect.

It is interesting that the reactivity toward iodonium ion of CH_3CO_2H and its anion are only approximately 2 log units apart. Accordingly, a solution having pH 2.8, in which 1% of the acid is ionized, would undergo equal amounts of alkylation via the anion and the neutral species. In our experiments alkylation via the anion would have been mostly suppressed in 0.01 M $HClO_4$ and completely suppressed in 1 M $HClO_4$. In a control experiment, in which HCO_2H–$HClO_4$ was added after the alkylation of CH_3CO_2H in 1 M $HClO_4$, less than 10% of the ester product was formate. Accordingly, esterification of iodopentanol is not a main source of esters in our alkylations.

The extraordinarily high nucleophilicity of un-ionized carboxylic acids in water presumably reflects anionic character in the hydrogen bonded complex with H_2O, 7. The dimer 8 is

R—C（=O）（O—H···H_2O）

7

R—C（=O···H—O）（O—H···O）C—R

8
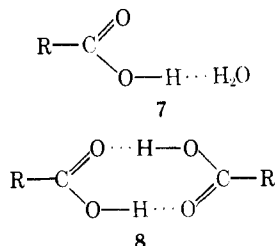
presumably a principal component of pure carboxylic acids. Since the reactivity of pure acids is approximately 1.6 log units less than that of the complex 7, one wonders whether the more reactive monomer, RCO_2H, may be the principal species alkylated in pure RCO_2H. For CH_3CO_2H, K_d (dimer ⇌ monomer) is 0.47×10^{-4} in cyclohexane and 2.4×10^{-4} in benzene.[23] If K_d is assumed to be 10^{-3} in the more polar acetic acid, approximately 1% monomer would be present. If monomer is as nucleophilic as the species 7 present in water, it may, in fact, be the principal species alkylated.

The data of Table IV indicate that in water solvent alcohols tend to be slightly more nucleophilic than H_2O. Among the alcohols studied, the relative nucleophilicities indicate that steric effects are dominant. Only t-BuOH shows a marked effect, approximately 1 log unit, relative to i-PrOH. The inductive substituent in $(CH_2OH)_2$ causes surprisingly little decrease (0.17 log units) in nucleophilicity. In contrast, the pK_a values in water of glycolic acid, $HOCH_2CO_2H$, and acetic acid, 3.83 and 4.76, respectively, differ by 0.93 log units.

Nucleophilicity of Mixed Solvents. For ethanol–water mixtures, the data in Table IV, footnote f, indicate that little variation in apparent higher nucleophilicity of ethanol, compared to H_2O, occurs over the range of composition studied. Published reports show that different results are observed for octyl halides and tosylate[24] and butyl bromide.[25] The cause

of variable $EtOH/H_2O$ selectivity in substitution reactions has been the subject of considerable speculation. For S_N1 reactions a selectivity–reactivity relationship sometimes occurs.[26] That such relationships are not generally found is indicated particularly by Ritchie's studies,[1,2,27] and by the results of the halonium ion competition reactions reported here. The slope, 0.77 (Figure 3), is approximately the sensitivity, relative to that for reactions of CH_3I expected for a primary reactant, 1, compared to a methyl derivative. The high reactivity of the positive halogen leaving group has not made the halonium ion appreciably less selective than otherwise expected.

It has been claimed[24] that the low $EtOH/H_2O$ selectivity observed in primary halide solvolyses is evidence that reactive primary carbonium ions, present as ion pairs, are intermediates in S_N2 reactions. This claim could possibly be extended to our reactions of iodonium ion 1, although the intermediate would be described as a solvated ion. We believe, however, that the claimed observation of low selectivity is fallacious. The selectivity in these reactions appears to be more appropriately represented by the overall response to nucleophilicity, including the nucleophilicity of anions, as is discussed in the next section of this paper. By this criterion, reactions of primary substrates are known to be among the more selective reactions. we suggest that variations in $EtOH/H_2O$ selectivity exhibited by systems such as benzhydryl halide solvolyses represent interactions which lead to modest perturbation of the results which are expected on the basis of nucleophilicity alone. The results of ref 24 may be interpreted as indicating that hydrophobic effects raise the tendency of ethanol to react with octyl substrates in highly aqueous solvents, for example. Solvent sorting in the vicinity of cations (which may reflect hydrophobic effects) has been discussed in relation to variable ROH/HOH reactivity.[26] All nucleophilicity scales, of course, reflect such effects, but the success of various correlation equations shows that overall trends are not obscured.

The Applicability of a Single Scale to Nucleophiles and Substrates of Varying Charge Type. The Swain–Scott equation (40) may be considered to be a reduced form of four-parameter equations such as 2 (cf. ref 3 and 4).
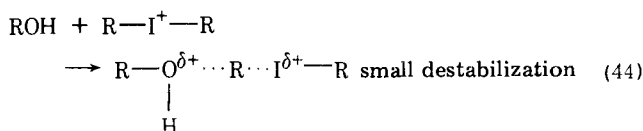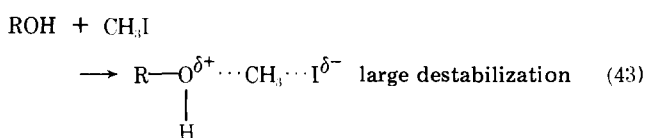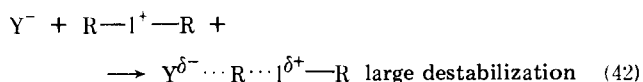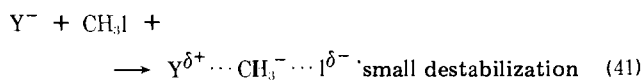
$$\log k/k_0 = sN \qquad (40)$$

Does a single set of compound parameters apply to both types of reactions (solvolyses and anionic S_N2 reactions)? Presently the two reactions have been treated separately. Schleyer's group has used the symbol l, instead of s, for the sensitivity to nucleophilicity in their four-parameter equation for solvolytic reactions, $\log k/k_0 = lN + mY$. In Table V a few sensitivity parameters are compared. The varying s values for PhCOCl almost certainly indicate that the mechanism of reaction changes toward nucleophilic addition for the anionic nucleophiles of the Swain–Scott study. For other compounds, the various scales are comparable, although benzyl may be expected to show variation of mechanism also.

The comparisons in Table V involve minimal variation of structure, since secondary substrates were not included in the Swain–Scott correlation. Data recently reported by Sukenik and Bergman[28] are of interest in this connection. Using water-soluble p-trimethylammonium benzenesulfonates, they determined the acetate/alcohol product ratios of Table VI in the presence of 1.0 N NaOAc in H_2O. Also shown in Table VI

are product ratios which we calculated using "average" s values, as well as the s values required to reproduce the product data (with $N = 2.7$). Examination of these results suggest that *solvolytic and anionic (Swain–Scott) sensitivities to nucleophilicity do not differ greatly*. Although complications are to be expected for compounds exhibiting pronounced S_N1 behavior, the use of available parameters for both S_N2 and solvolytic reactions appears to constitute a useful approximation.

The reactions of methyl iodide and of pentamethyleneiodonium ion with anionic and neutral nucleophiles in water fall into four charge types for reactants and transition states. These are illustrated in eq 41–44. Also shown is the presumed effect

$$Y^- + CH_3I +$$
$$\longrightarrow Y^{\delta+} \cdots CH_3^- \cdots I^{\delta-} \text{ 'small destabilization} \quad (41)$$

$$Y^- + R\text{---}I^+\text{---}R +$$
$$\longrightarrow Y^{\delta-} \cdots R \cdots I^{\delta+}\text{---}R \text{ large destabilization} \quad (42)$$

$$ROH + CH_3I$$
$$\longrightarrow R\text{---}O^{\delta+} \cdots CH_3 \cdots I^{\delta-} \text{ large destabilization} \quad (43)$$
$$\qquad\qquad |$$
$$\qquad\qquad H$$

$$ROH + R\text{---}I^+\text{---}R$$
$$\longrightarrow R\text{---}O^{\delta+} \cdots R \cdots I^{\delta+}\text{---}R \text{ small destabilization} \quad (44)$$
$$\qquad\qquad |$$
$$\qquad\qquad H$$

on the transition state, relative to the reactant, of using a solvent of high dielectric constant, as quoted in most physical organic textbooks. The differential solvent effect of the change from CH_3I to $R\text{-}I^+\text{-}R$ is as follows: small destabilization to large destabilization for anions, Y^-, and large stabilization to small destabilization for uncharged nucleophiles, ROH. Although these designations are only intuitive, they do indicate that different solvent effects may be expected for the two types of nucleophiles.

The above analysis suggests that it would be an unusual accident if a single nucleophilicity scale suffices for both types of substrates in a particular solvent. Nevertheless, Figure 3 indicates that this unlikely result is found, although the large deviation for CN^- reminds us of the limitations of our correlation. From another point of view, we may focus on the largest charge–charge interaction, the attraction between Y^- and $R\text{-}I^+\text{-}R$. There is no indication that reactions of these species are favored, resulting in an upward displacement (Figure 3) of points for anions, relative to the point for H_2O. The results suggest that *nucleophilicities are not dependent on the charge type of the substrate*, at least for reactions in water. Clearly the range of applicability of the often-quoted rules regarding eq 41–44 is deserving of reexamination.

In a comparable observation to that mentioned above, Ritchie[2,27] has noted that N^+ substrates behave similarly toward anionic, cationic, and uncharged nucleophiles. The observation has been a factor prompting him to abandon the hypothesis that the transition states for N^+ reactions are characterized by desolvation of the anion, but not of the cation. Earlier, anionic desolvation was pictured to occur as a result of attraction between anions and cations over relatively long distances.

A sweeping generalization of the phenomena which have been mentioned would be that electrostatic interactions involving nucleophiles play a negligible role in ionic reactions, at least for hydroxylic solvents. If so, extensive charge delocalization into the bulk of the solvent would explain the results. We have previously reported what we believe to be important

and strong evidence for the ability of solvent to delocalize negative charge.[29] In our study, long-range interactions were observed in steroidal tosylate solvolyses. The large effect of substituents at C-17 upon the solvolytic transition state at C-3 could only be accommodated if the $C^+\text{-}OTs^-$ dipole of the transition state (or the substituent dipole) behaved as a charge. This behavior would occur if the negative end of the dipole were delocalized to a large distance through alignment of solvent dipoles, including hydrogen bonds.

We suggest that the charge distribution around reacting nucleophiles is similar for anions and formally uncharged species, and that the distribution arises predominantly from the orientation of solvent molecules. This hypothesis opens the way to a reconsideration of the role of desolvation in the transition state of N^+ reactions. Long-range bonding is a possible replacement for electrostatic attraction as the driving force of nucleophile–substrate interactions during desolvation.

Experimental Section

Pentamethyleneiodonium Hexafluoroantimonate (1). The isolation of the solid ion salt obtained from the dihalide and $CH_3F\text{-}SbF_5\text{-}SO_2$ (methylated sulfur dioxide)[30] was not described in our earlier publication.[3] Methyl fluoride (Columbia Organic Chemicals, 3260 mL, 0.13 mol) was added from a 2-L gas buret to SbF_5 (21.68 g, 0.1 mol) in approximately 80 mL of SO_2. Our water-filled buret was connected by a stopcock to a water tap which is turned on to drive the CH_3F through a drying tube and then through a gas inlet tube whose tip is above the surface of the dry ice cooled, magnetically stirred, SO_2 solution. In early experiments any unabsorbed exit gases were measured in a second gas buret. A small amount of nonabsorbable gas (nitrogen?) was found which blocks absorption in the absence of the "driver" buret system.

1,5-Diiodopentane (32.39 g, 0.1 mol) was added in approximately 3-mL portions to the magnetically stirred methylated sulfur dioxide, initially at -60 °C. The temperature in the exothermic reaction was not allowed to rise above -45 °C. Although we used a jacketed vessel cooled by a circulating low-temperature bath, a dry ice bath can be used for the reaction. The vessel was brought to -30 °C for 1 h. Cooled methylene chloride (140 mL) was added. Cloudiness was noted and the temperature was found to be -40 °C. An additional 200 mL of cold (-60 °C) methylene chloride was added in portions. The precipitated iodonium salt was filtered in a -65 °C box using a pressure filtration apparatus consisting of a medium porosity sintered glass filter in the bottom of a 250-mL reservoir containing a neck fitted with ball joint and clamp. This apparatus was left at -65 °C for 12 h while a very slow flow of nitrogen was admitted. The white solid was broken up (loose, light lumps) and transferred to a long tube fitted with a ball joint. The tube was evacuated for 8 h at -30 °C by a vacuum pump protected with a liquid nitrogen trap. (It is likely that a shorter period of pumping at 0 °C could be used.) The yield was 27.2 g, 63%, of material which broke into a white, crystalline powder upon shaking.

Reaction of Pentamethyleneiodonium Ion with Nucleophiles. After early experiments using 0.1-g portions of iodonium salt and small volumes of aqueous nucleophile, our experiments were repeated with the following procedure. The iodonium ion salt **1**, stable indefinitely in a screw cap jar at -65 °C, was placed in a dry bag which had been flushed with N_2 for 15 min. When the frost dried, the flow of nitrogen was reduced, and the ion was transferred with a spatula to vials which had been filled with N_2 in the dry bag, corked and weighed outside of the dry bag. The vials were reweighed to verify that 0.3–0.4 g of ion had been transferred. (The white iodonium salt readily survived repeated warming to near room temperature and weighing at room temperature.) The vials were returned to the -65 °C box.

Nucleophile salts were mixed from 2 M stock solutions, using graduated cylinders or syringes, and made up to 100 mL with H_2O if one nucleophile was at less than 1 M final concentration. The solution, contained in a 250-mL Erlenmeyer flask, was brough to 25 $\pm$ 0.3 °C and stirred at maximum speed with a magnetic bar. The cold, powdered iodonium salt was added in one portion from the vials, which had been prepared from glass tubing to obtain an unconstricted neck. A control experiment in one instance showed that ion warmed to room temperature gave the same reaction products, although it did not

disperse quite as readily. The ion appeared to form a clear solution from which cloudy reaction product began to separate immediately.

Analysis of Reaction Products. For reactions in which iodopentanol was not formed, deuteriochloroform (2–3 mL) was added to the stirred solution, which was transferred to a separatory funnel and shaken. The small amount of CDCl$_3$ extract was removed with a long-nosed "NMR" pipet, centrifuged, and analyzed by NMR at 90 MHz. The triplet region was spread to 300 Hz and integrated to obtain the relative amounts of products.

For reactions involving H$_2$O or OH$^-$ as a nucleophile, approximately two or three additional extractions were required to remove 5-iodo-1-pentanol from the water layer. After several efforts to esterify the alcohol in situ, we elected to extract twice with 20-mL portions of CHCl$_3$. The dried extract (molecular sieve 5a, 30 min) was distilled at 120–130 mm (20–25 °C), using a Vigreux column and a condenser cooled to −20 °C with a circulating bath. When the distillation of CHCl$_3$ was nearly complete the undistilled product was removed with a small amount of CDCl$_3$, centrifuged, and analyzed by NMR (90 MHz).

5-Iodo-1-pentanol is expected to undergo ready cyclization in basic solutions. Accordingly reaction mixtures involving OH$^-$ were acidified with 15 mL of 7 N H$_2$SO$_4$, and then cooled to approximately 15 °C before extraction. The presence of unreacted particles of halonium ion salt would lead to false high values for halide nucleophilicity by reaction after acidification. Accordingly a 2-min reaction time, instead of 1 min, was used. An extract of iodopentanol which stood for 1 week in CHCl$_3$–molecular sieve showed an absence of iodopentanol upon workup. Accordingly short drying periods were used. There is still uncertainty concerning whether iodopentanol quantitatively survives our isolation procedure. The variable values for the reactivity of OH$^-$ (Table III) may arise, in part, from analytical difficulties. In calculating the reactivity of OH$^-$, the area for CH$_2$O of bis(5-iodo-1-pentyl) ether (**2**) was divided by two and added to the area for CH$_2$O of 5-iodo-1-pentanol (**3**). It is assumed that **2** arises from initially formed **3** or its anion in a reaction which is irrelevant to the reactivity of OH$^-$.

Owing to overlap between NMR peaks of RCH$_2$OH and RCH$_2$Cl, and also between RCH$_2$Br and [I(CH$_2$)$_5$]$_2$O, CDCl$_3$ solutions of these species were analyzed with the aid of trifluoroacetylation (for ROH) and acid-induced shift (ROR) (cf. Figure 2).[32] An amount of CF$_3$CO$_2$H approximately equal to that of the CDCl$_3$ solution was added to the NMR tube, followed by CF$_3$SO$_3$H (approximately 5 mm in the tip of a glass disposable pipet).

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