solvents with conformational changes are fraught with ambiguity. We have found this to be true for all the polyamine and amino acid complexes we have investigated and we suppose that the problem is quite general to these systems.

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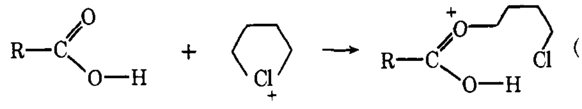
Solvents of Low Nucleophilicity. XIV. A Nucleophilicity Scale Based on Rates of Reaction of Tetramethylenechloronium Ion with Carboxylic Acids and Its Use in Swain-Scott Type Correlations

Sir:

Various halonium ions recently have been prepared as stable species, some of which undergo extraordinarily facile alkylation reactions.[1] We now report (in Table I) the rate constants for the reaction of tetramethylenehalonium ions with various carboxylic acids in SO_2 at $-65.6 \pm 0.1°$ (eq 1). The logarithms of



(1)

these rate constants, given in Table I, are particularly significant as possible measures of the nucleophilicities of the carboxylic acids. They are comparable to log *k* values for solvolysis of *tert*-butyl chloride, used as measures of ionizing power.[2]

Table I. Rate Constants for Reactions of Tetramethylenechloronium Ion with Nucleophiles in SO_2, $-65.6 \pm 0.1°$

Nucleophile	$k_{1/2}$, $M^{-1/2}$ sec^{-1} [a]	Log k
HCO_2H	5.6×10^{-2}	-1.25
CH_3CO_2H	4.1×10^{-2}	-1.39
$ClCH_2CO_2H$	4.2×10^{-3}	-2.38
Cl_2CHCO_2H	2.3×10^{-4}	-3.64
CF_3CO_2H	8.7×10^{-6}	-5.06

[a] Calculated from the integrated rate equation for reactions first order in halonium ion and half order in nucleophile. The approximate half-order dependence, demonstrated in six runs for acetic acid, may result from the acid dimer-monomer equilibrium.

Winstein, Grunwald, and Jones, and Swain and Scott have considered solvolysis rates to be primarily a function of the nucleophilicity and the ionizing power of the solvent.[3] The Swain-Scott equation may be written in the form

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

In this equation giving logarithms of rate constants, *k*, for solvolyses in solvents A and B, $N_A{}^B$ and $Y_A{}^B$ are the differences in nucleophilicities and ionizing powers,

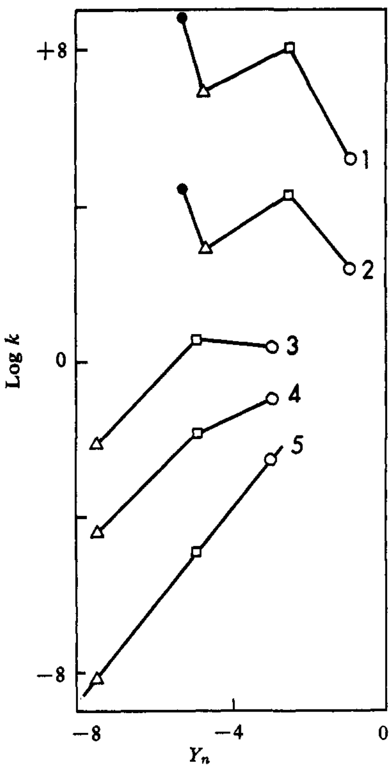


Figure 1. Log *k* for alkyl tosylates plotted against Y_n for the solvents CF_3CO_2H (○), CH_3CO_2H (△), HCO_2H (□), and EtOH (●). The alkyl tosylates, identification numbers, solvolysis temperatures, and number of log units by which the graph has been displaced upward are, respectively: methyl, 1, 75°, 13 units; ethyl, 2, 75°, 9 units; isopropyl, 3, 25°, 5 units; 3-heptyl, 4, 25°, 2 units; 2-adamantyl, 5, 25°, 0 units.

respectively, between the two solvents, and *m* and *s* are sensitivity parameters characteristic of the compound.

Swain, Mosely, and Bown[4] used the relationship of eq 2 in the form given in eq 3. However, the results

$$\log (k/k_0) = c_1d_1 + c_2d_2 \qquad (3)$$

stemming from their assumptions regarding standard reaction parameters were not fully understood.

Accordingly, in addition to developing our own parameters for use in eq 2, we have derived eq 4–7 for converting the Swain-Mosely-Bown parameters into *s*, *N*, *m*, and *Y* values as defined for eq 2, based on the assumptions that $s = 0$ for *tert*-butyl chloride, $s = 1$ for methyl bromide, and that the *N* values for acetic and formic acid are equal.

$$Y_{SMB} = d_1 + d_2 \qquad (4)$$

$$m_{SMB} = 0.11(c_1 - c_2) + c_2 \qquad (5)$$

$$N_{SMB}/0.53 = 0.89d_2 - 0.11d_2 \qquad (6)$$

$$s_{SMB} = (c_1 - c_2)/0.53 \qquad (7)$$

For treatment of solvolyses in acid solvents, including trifluoroacetolyses, according to eq 2, availability of data led us to choose the logarithms of the rate constants for the solvolysis of neophyl tosylate (p-$CH_3C_6H_4SO_3$-$CH_2C(CH_3)_2(C_6H_5)$) as the measures of ionizing power. These values, here designated Y_n, have been shown to be

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[1] (a) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **92**, 2562 (1970); (b) P. E. Peterson, P. R. Clifford, and F. J. Slama, *ibid.*, **92**, 2840 (1970).

[2] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

[3] (a) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); (b) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

[4] C. G. Swain, R. B. Mosely, and D. E. Bown, *ibid.*, **77**, 3731 (1955).

Table II. Comparison of Swain–Scott Type Compound Parameters from Various Sources

R	$m_{PW}/1.451$ ROTs	m_{SMB} RBr	m_{AF} ROTs	m_{EW} ROTs	s_{PW} ROTs	s_{SMB} RBr	s_{SMB} ROTs
Methyl	0.30[a]	0.33	0.30[a,b]	0.23[a,c]	0.9[a]	1.00	
Ethyl	0.41[a]	0.41	0.37[a,b]	0.25[d,c]	0.75[a]	0.83	0.77
Propyl	0.39[a,e]				0.71[a]	0.81[f]	
Isobutyl	0.36[a,e]				0.65[a]		
Isopropyl	0.70[g]	0.62	0.72[g,h]	0.42[g,c]	0.58[g]	0.60	0.28[i]
2-Butyl	0.68[g]		0.70[g,j]		0.39[g]		
3-Heptyl	0.70[g]		0.71[g,j]		0.28[g]		
2-Adamantyl	0.88[g]		0.89[g,c]	0.91[g,c]	0.0[g]		

[a] 75°. [b] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 64. [c] Reference 6b. [d] 50°. [e] The m value was calculated using the estimated value for k_s, which reflects solvolysis without neighboring group participation; *cf.* I. L. Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91,** 5635 (1969). [f] *n*-Butyl. [g] 25°. [h] Reference 6d. [i] Brosylate. [j] P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87,** 5169 (1965).

Table III. Comparison of Solvent Nucleophilicity Scales

Nucleophile	N_{PW}[a]	N_{SMB}	N_{SFLL}[b]	N_{SS}[c]
I^-				5.04
HO^-				4.20
$CH_3CO_2^-$				2.72
EtOH, 100%	0.76[d]	−0.19	0.9	
80%	0.00[d]	0.00	0.00	
50%			−0.80	
H_2O		−0.44		0.00
MeOH		+0.02		
Acetone, 90%		−0.16		
50%		−0.06		
Formic acid	−1.52	−2.46	−1.60	
Acetic acid	−1.66	−2.46	−1.00	
Chloroacetic acid	−2.65			
Dichloroacetic acid	−3.91			
Trifluoroacetic acid	−5.33		−4.35	

[a] Values from Table I referenced to 80% EtOH by subtracting 0.27. [b] Reference 6d; values scaled to 80% EtOH. [c] Reference 3b. [d] Based on methyl tosylate solvolysis data s and m values (PW) from Table II.

insensitive to nucleophilicity, since the solvolyses proceed by phenyl participation pathways.[5]

Rearranging eq 2 yields eq 8, which indicates that for

$$\log (k_A/k_B) = m[(s/m)N_A{}^B + Y_A{}^B] \qquad (8)$$

a series of compounds having increasing s values plots of log k *vs.* Y may be increasingly nonlinear. The hindered secondary, primary, and methyl tosylates fulfill this expectation (*cf.* Figure 1), confirming the influence of nucleophilicity upon solvolytic rates[6] in carboxylic acid solvents.

By adding the term, $(s/m)N$, to the ordinates, the nonlinear plots of Figure 1 may be corrected to straight lines for log k data in acetic, formic, and trifluoroacetic acid (designated log k^A, log k^F, and log k^T). It may be shown that s/m is given by eq 9. Using this value of s/m, we obtain m and s by application of eq 8. The resulting values, designated m_{PW} and s_{PW} are given in Table II, along with the Swain–Mosely–Bown values and values obtained from data for *tert*-butyl chloride reacting in acetic–formic acids (AF) and ethanol–water (EW).

$$\frac{s}{m} = \frac{\begin{array}{c}[(Y^F - Y^A)/(\log k^F - \log k^A) - \\ (Y^A - Y^T)/(\log k^A - \log k^T)]\end{array}}{\begin{array}{c}[(N^A - N^T)/(\log k^A - \log k^T) - \\ (N^F - N^A)/(\log k^F - \log k^A)]\end{array}} \qquad (9)$$

In Table III both sets (PW and SMB) of the previously unavailable nucleophilicity parameters, N, are tabulated, along with a scale recently suggested by Schleyer, Fry, Lam, and Lancelot[6d] and some ion nucleophilicity values of Swain and Scott.[3b]

The approximate agreement among various parameters shown in Tables II and III should encourage further exploration of the approaches outlined here and elsewhere.[7]

Acknowledgment. We thank Professor Paul Schleyer for informing us of his alternative treatment (accompanying communication[7]). D. Warren Vidrine contributed to the derivation of eq 4–7. Support by the National Science Foundation (Grant No. GP 10919) is gratefully acknowledged.

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(5) (a) A. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, **90,** 6546 (1968); (b) A. H. Fainberg and S. Winstein, *ibid.*, **78,** 2763 (1956).

(6) (a) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *ibid.*, **89,** 5902 (1967); (b) J. L. Fry, C. J. Lancelot, L. K. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92,** 2538 (1970); (c) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92,** 2540 (1970); (d) P. v. R. Schleyer, J. L. Fry, L. K. Lam, and C. J. Lancelot, *ibid.*, **92,** 2542 (1970).

(7) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, **94,** 992 (1972).

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Correlation of Solvolysis Rates with Three- and Four-Parameter Relationships. A Scale of Solvent Nucleophilicities

Sir:

It was recognized 20 years ago[1] that the effect of variation of solvents on solvolysis rates might be correlated by an equation of the type[1–3]

$$\log (k/k_0) = lN + mY \qquad (1)$$

Here l and m are substrate sensitivity factors; Y is a measure of the "ionizing power" of the solvent and N of its "nucleophilicity." However, this equation

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(1) S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, **73,** 2700 (1951).

(2) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79,** 4146 (1957).

(3) For a critical review of the background to this paper, see A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 43–49, 63–66.