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Application of the aromatic ring parameter (*I*) to solvolyses of extremely crowded alkyl derivatives

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Abstract

The solvent dependences of the specific rates of solvolysis of 4-chloro-2,2,4,6,6-pentamethylheptane (**2**) and 3,3-dimethyl-1-neopentylbutyl mesylate (**3**), previously analyzed using the extended Grunwald-Winstein equation with incorporation of N_T and Y_X values, are better correlated using a combination of Y_X and I values; a claim of assistance from Brønsted-base-type solvation during solvolyses of adamantyl derivatives is discussed.

Keywords: Grunwald-Winstein equation; solvolysis

Use of the extended Grunwald-Winstein equation[1] (Eq. 1) has demonstrated that the solvolyses

$$\log (k / k_0)_{RX} = lN_T + mY_X + c \qquad (1)$$

of tertiary alkyl derivatives frequently exhibit a modest sensitivity towards changes in solvent nucleophilicity. In Eq. 1, k and k_0 are the specific rates of solvolysis of the RX substrate in a given solvent and in the standard solvent (80% ethanol), respectively; l is the sensitivity towards changes in solvent nucleophilicity (N_T)[2]; m is the sensitivity towards changes in solvent ionizing power (Y_X, for leaving group X)[3]; and c is a constant (residual) term.

If one carries out a simple Grunwald-Winstein equation treatment (Eq. 1, without the lN_T term), the presence of a sensitivity towards solvent nucleophilicity leads to the data points for solvents rich in fluoroalcohol (high Y_X, low N_T) lying *below* the correlation line.[4] Increased steric hindrance to rearside nucleophilic solvation reduces these deviations[5,6] and, for example, the appreciably hindered 2-chloro-2,4,4-trimethylpentane as substrate leads to the fluoroalcohols lying on the correlation line and to an extended equation l value of 0.00 ± 0.02.

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There are also many instances where simple Grunwald-Winstein plots lead to the points for solvents rich in fluoroalcohol lying *above* the correlation line. These plots have been largely observed for solvolyses of substrates with one or more aromatic rings entering into conjugation with the developing carbocationic center.[7] This behavior can be treated by the addition of a new term to Eq. 1, to give Eq. 2. The additional term involves the sensitivity h to changes in the aromatic ring parameter (I). Frequently, but

$$\log (k / k_0) = lN_T + mY_X + hI + c \tag{2}$$

not always, an appreciable hI contribution is accompanied by a negligible lN_T contribution, and Eq. 3 can be employed. The vast majority of the applications of the I scale have involved substrates

$$\log (k / k_0) = mY_X + hI + c \tag{3}$$

with aromatic rings on the α-carbon,[7] or on the β-carbon but migrating to the α-carbon during solvolysis[8]; an alternative approach to the analyses,[9] in terms of Y_X and $Y_{\Delta X}$ scales, was shown[8] to be equivalent to an analysis in terms of Y_X and I scales. Eq. 3 has been applied,[10] with relatively low h values, to solvolyses with alkenyl or alkynyl substituents attached to the α-carbon.[11]

Recently, Eq. 3 has been used in analysis of the specific rates of the solvolysis-decomposition of *N*-(1-adamantyl)-*N*-*p*-tolylcarbamoyl chloride [1-Ad(p-$CH_3C_6H_4$)NCOCl, **1**).[12] The good fit using Eq. 3 is surprising, because the aromatic ring present cannot enter into conjugation with the developing carbocationic center.

A report concerning the specific rates of solvolysis of two highly hindered substrates, the tertiary 4-chloro-2,2,4,6,6-pentamethylheptane (**2**) and the secondary 3,3-dimethyl-1-neopentylbutyl mesylate (**3**) has recently appeared.[13] The data points for the solvents rich in fluoroalcohol again lie *above* the correlation line, the first instance where this has been observed for simple (unsubstituted) alkyl derivatives. As one would predict, when Eq. 1 was applied, negative l values were observed. These were rationalized in terms of a more intense incipient carbocation solvation of the Brønsted base type[14] in solvolyses of the standard adamantyl substrates than in the solvolyses of **2** and **3**. This corresponds to a contribution towards the solvolyses used to establish the Y_X scales involving increased specific rates with increases in solvent nucleophilicity.

To investigate this possibility, one would like to eliminate the dominant influence of solvent ionizing power on the specific rates of solvolysis of initially neutral adamantyl derivatives. The required study has already been carried out using the 1-adamantyldimethylsulfonium ion as substrate.[15] The specific rates of solvolysis varied by a factor of less than seven over 41 solvolyses in solvents of widely varying character and, further, the faster reactions were in the least nucleophilic fluoroalcohol solvents. This strongly suggests that, while the proposed Brønsted base type solvation almost certainly exists,[14] it is just one of several minor effects which can be neglected in the context of linear free energy relationships.

An alternative approach is to apply Eq. 3. This has been done with the exclusion of the data for acetic acid (no I value available). In Table 1, the analyses are presented using Y_X alone and in conjunction with either N_T or I. The correlations with N_T and Y_X are essentially identical to those reported earlier with the one additional solvent.[13] In these earlier studies, Y_{OTs} values were used in the analyses of the specific rates of solvolysis of **3**; we have, in addition, used what would appear to be more appropriate Y_{OMs} values. Surprisingly, slightly better correlations are obtained with use of Y_{OTs}. It can be seen from inspection of Table 1 that the best correlations, in terms of all of the listed measures of goodness of fit, are when a combination of Y_X and I scales is used.

Table 1

Correlation of the specific rates of solvolysis,[a] at 25.0°C, of 4-chloro-2,2,4,6,6-pentamethylheptane (**2**) and 3,3-dimethyl-1-neopentylbutyl mesylate (**3**), using simple and extended (two-term) forms of the Grunwald-Winstein equation.

Scales[b]	n[c]	l[d]	m[d]	h[d]	c[e]	R[f]	F[g]
Compound 2:							
Y_{Cl}	10		0.73 ± 0.06		0.17 ± 0.33	0.9716	135
N_T, Y_{Cl}	10	-0.32 ± 0.08	0.54 ± 0.06		0.04 ± 0.20	0.9914	200
Y_{Cl}, I	10		0.75 ± 0.03	1.14 ± 0.17	0.10 ± 0.13	0.9961	447
Compound 3:							
Y_{OMs}	12		0.68 ± 0.05		0.12 ± 0.29	0.9719	170
N_T, Y_{OMs}	12	-0.24 ± 0.05	0.47 ± 0.05		-0.01 ± 0.17	0.9919	274
Y_{OMs}, I	12		0.64 ± 0.02	0.87 ± 0.13	0.05 ± 0.13	0.9952	461
Y_{OTs}	12		0.78 ± 0.05		0.02 ± 0.22	0.9838	302
N_T, Y_{OTs}	12	-0.19 ± 0.05	0.59 ± 0.06		-0.05 ± 0.14	0.9939	366
Y_{OTs}, I	12		0.74 ± 0.02	0.67 ± 0.11	-0.02 ± 0.10	0.9971	777

[a] Data from ref. 13.

[b] The parameters used in the analyses.

[c] Number of solvents (data points).

[d] With associated standard error, in all instances the probability that the contribution to the linear free energy relationship was insignificant was less than 0.006.

[e] Constant (residual) term, accompanied by the standard error of the estimate.

[f] Correlation coefficient.

[g] F-test value.

When the I scale was initially developed,[10] it was suggested that the magnitude of the values could be, at least in part, governed by perturbations associated with reductions in the extent of ion-pair return to reactant. In the solvolyses of **2** and **3**, it is observed[13] that the major products are those of elimination (94%–98%), whereas the standard substrates give 100% substitution. If return with attack at hydrogen occurs at the intimate ion-pair stage,[16,17] this now corresponds to product formation and the pattern of ion-pair return to reactant is to be expected to differ from that for the solvolyses used to establish the Y_X scale. In a parallel manner, perturbations are to be expected to result from the loss of phenyl isocyanate preventing internal return to reactant during solvolyses of **1** in the fluoroalcohol-rich solvents.[12]

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