Solvent Effects on Solvolytic Reactivity. A Diagnostic Test for Neighboring-Group Assistance by σ Conjugation in Solvolysis Reactions

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The solvolysis rates of 13 arenesulfonates have been determined in mixtures of ethanol and water (the E-series solvents) and acetic acid and formic acid (the A-series solvents). The substrates studied include the following: neophyl (1), 2-adamantyl (2), neopentyl (3), and cyclooctyl (4) tosylates; cyclopropylcarbinyl pemsylate (5a) and tosylate (5b); *exo*-2-norbornyl tosylate (6); cyclobutylcarbinyl (7), cyclobutyl (8), and pinacolyl (9) brosylates; cyclopentyl (10), cyclohexyl (11), and 2-propyl (12) tosylates; and cyclopentylcarbinyl brosylate (13). Correlations of the rate data by eq 1 [log k_t(Y) = a + b log k_t(neophyl–OTs)] showed that the various substrates responded differently to the examined solvent effects on the solvolytic reactivity. For compounds 2–4, linear correlations were obtained. For compounds 5–9, E-line, A-line dispersions were noted which diverged with increasing ionizing power; for compounds 10–12, parallel E-line, A-line dispersions were obtained; and for compound 13, an E-line, A-line dispersion was observed which converged with increasing ionizing power. Statistical analyses of the rate data correlations confirmed the significance of the E or A classification of data. The results are interpreted in terms of differences in the involvement of solvent in the transition state for those solvolyses assisted by bridging from those assisted by C–C σ bond hyperconjugation.

In our study[1] of solvent effects upon rates of solvolysis of selected arenesulfonates whose solvolytic behavior suggests anchimeric assistance by C–C σ bonds,[2] we use a linear free energy relationship (eq 1)[3] to analyze our data.

$$\log k_t(\text{Y}) = a + b \log k_t(\text{neophyl–OTs}) \qquad (1)$$

As a result of such analyses, we have observed[1d–f] what appears to be a characteristically different response to a solvent effect by substrates ionizing with neighboring-group assistance by σ conjugation[2] from those ionizing with assistance by bridging.[4] The basis for this proposal rests upon several factors: e.g., (1) the assumption that the solvolyses of neophyl tosylate are a good model for k_Δ (bridging) mechanistic behavior,[3a,5] (2) the assumption that *exo*-2-norbornyl tosylate solvolyzes without rearside nucleophilic solvent assistance,[6,7] (3) the finding that correlations of rate data by eq 1, in two hydroxylic solvent series, E and A,[8] for compounds 5–7 yield an E-line, A-line dispersion,[9] and (4) the recognition that the pattern of this

dispersion, D (divergent with increasing ionizing power), contrasts with the patterns C and P (convergent with increasing ionizing power, and parallel) observed for substrates known to solvolyze by competitive k_s–k_Δ processes (13–14) and by the k_s process (10–12), respectively.

In order to evaluate the validity of this rate data response to solvent effect, it is necessary to analyze statistically the correlations obtained by use of eq 1 for an extended data set of solvolysis rates. We now report for a wide variety of model compounds kinetic data where the number of data points collected in the two solvent series E and A have been doubled.

Results

New kinetic data for solvolyses of compounds 1–13 are shown in Table I. The course of reaction was followed by titrating the liberated arenesulfonic acid, and with the exception of compounds 5 and 8, it was observed that each reaction followed strictly first-order kinetic law up to at least 75% conversion, furnishing, within experimental error, 100% of the theoretical amount of acid present. Both cyclopropylcarbinyl pentamethylbenzenesulfonate (5a) and *p*-toluenesulfonate (5b) undergo solvolysis reactions accompanied by internal-return isomerization[1a,d] in all solvents investigated, as does cyclobutyl *p*-bromobenzenesulfonate (8) in acetic acid.[10] Therefore, the apparent first-order rate constants for these three compounds were calculated on the basis of acid liberated at ten half-lives, and, consequently, are a sum of the isomerization and solvolysis rate constants.[11]

In Table II is presented the requisite kinetic data for the correlations by the Winstein–Grunwald equation and the multiple regression analyses by the SAS General Linear Models. The results of these correlations and analyses are given in Tables III and IV.

Discussion

Correlations of Rate Data by the Winstein–Grunwald Equation. The solvent parameters derived from the

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(5) (a) Smith, S. G.; Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1961**, *83*, 618. (b) Shiner, V. J., Jr.; Serb, R. C. *Ibid.* **1976**, *98*, 862. (c) Ando, T.; Kim, S.-G.; Matsuda, K.; Yamataka, H.; Yukawa, Y.; Fry, A.; Lewis, D. E.; Sims, L. B.; Wilson, J. C. *Ibid.* **1981**, *103*, 3505.

(6) For leading references, see: Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977.

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(8) E = aqueous ethanol series; A = acetic acid–formic acid series of solvents.

(9) For a discussion of "dispersion", see: (a) Kosower, E. M. "Physical Organic Chemistry"; Wiley: New York, 1968; pp 318–319. (b) Streitwieser, A., Jr. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962; p 171.

(10) Roberts, D. D. *J. Org. Chem.* **1972**, *37*, 1510.

(11) Servis, K. L.; Roberts, J. D. *Tetrahedron Lett.* **1967**, 1369.

(12) (a) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963. (b) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.

Table I. Solvolysis Rate Constants Determined in This Study

compd[a]	solvent[b]	concn, 10^2 M		k,[c] s^{-1}	
		45 °C	25 °C	45 °C	25 °C
neophyl–OTs (1)	60E	0.8	1.0	$(5.14 \pm 0.05) \times 10^{-6}$	$(3.2 \pm 0.03) \times 10^{-7}$
	50E		0.08		$(5.83 \pm 0.05) \times 10^{-7}$
	40E	0.064	0.07	$(3.3 \pm 0.2) \times 10^{-5}$	$(1.92 \pm 0.05) \times 10^{-6}$
	75A	2.0	2.0^d	$(5.8 \pm 0.1) \times 10^{-6}$	$(7.5 \pm 0.08) \times 10^{-7\,d}$
	65A	2.0	2.0	$(1.06 \pm 0.01) \times 10^{-5}$	$(8.33 \pm 0.08) \times 10^{-7}$
	50A	2.0	2.0	$(2.2 \pm 0.01) \times 10^{-5}$	$(1.34 \pm 0.05) \times 10^{-6}$
	25A	2.0	2.0^d	$(5.5 \pm 0.2) \times 10^{-5}$	$(8.9 \pm 0.2) \times 10^{-6\,d}$
2-ada–OTs (2)	40E		0.064		$(2.25 \pm 0.05) \times 10^{-6}$
	75A	2.0	2.0^d	$(2.24 \pm 0.02) \times 10^{-6}$	$(2.60 \pm 0.02) \times 10^{-7\,d}$
	50A	2.0	2.0^d	$(1.58 \pm 0.01) \times 10^{-5}$	$(2.07 \pm 0.01) \times 10^{-6\,d}$
	25A	2.0	2.0^d	$(7.8 \pm 0.2) \times 10^{-5}$	$(1.05 \pm 0.03) \times 10^{-5\,d}$
neopentyl–OTs (3)	60E	1.6^e	1.0^f	$(1.25 \pm 0.01) \times 10^{-6\,e}$	$(1.00 \pm 0.03) \times 10^{-7\,f}$
	50E	2.0	1.0^f	$(5.0 \pm 0.06) \times 10^{-8}$	$(2.61 \pm 0.02) \times 10^{-7\,f}$
	40E	0.08		$(1.2 \pm 0.06) \times 10^{-7}$	
	75A	2.0^e	2.0^f	$(8.3 \pm 0.1) \times 10^{-7\,e}$	$(5.2 \pm 0.1) \times 10^{-8\,f}$
	50A	2.0	2.0^f	$(7.83 \pm 0.06) \times 10^{-8}$	$(2.54 \pm 0.02) \times 10^{-7\,f}$
	25A	2.0^e	2.0^f	$(8.3 \pm 0.3) \times 10^{-6\,e}$	$(8.1 \pm 0.2) \times 10^{-7\,f}$
c-C$_8$H$_{15}$–OTs (4)	90E		3.0		$(3.08 \pm 0.05) \times 10^{-5}$
	70E		2.0		$(2.55 \pm 0.07) \times 10^{-4}$
	50E		0.2		$(1.2 \pm 0.05) \times 10^{-3}$
	40E		0.08		$(6.5 \pm 0.3) \times 10^{-3}$
	75A		2.0		$(5.18 \pm 0.08) \times 10^{-4}$
	50A		2.0		$(3.00 \pm 0.07) \times 10^{-3}$
	25A		2.0		$(1.15 \pm 0.03) \times 10^{-2}$
c-PrCar–OPms (5a)	70E		0.3		$(8.5 \pm 0.1) \times 10^{-4}$
	60E		0.1		$(2.8 \pm 0.06) \times 10^{-3}$
	50E		0.08		$(6.0 \pm 0.1) \times 10^{-3}$
	75A		2.0		$(7.2 \pm 0.2) \times 10^{-4}$
	65A		2.0		$(1.56 \pm 0.02) \times 10^{-3}$
	50A		2.0		$(4.4 \pm 0.2) \times 10^{-3}$
	25A		2.0		$(1.25 \pm 0.1) \times 10^{-2}$
c-PrCar–OTs^g (5b)	70E		1.0		$(3.5 \pm 0.2) \times 10^{-3}$
	60E		0.8		$(1.1 \pm 0.1) \times 10^{-2}$
	50E		0.6		$(2.5 \pm 0.05) \times 10^{-2}$
	75A		4.0		$(2.9 \pm 0.1) \times 10^{-3}$
	65A		0.8		$(6.4 \pm 0.09) \times 10^{-3}$
	50A		0.94		$(1.74 \pm 0.06) \times 10^{-2}$
	25A		1.2		$(4.6 \pm 0.8) \times 10^{-2}$
exo-2-norbornyl–OTs (6)	70E		0.24		$(6.58 \pm 0.05) \times 10^{-4}$
	60E		0.16		$(1.85 \pm 0.05) \times 10^{-3}$
	50E		0.08		$(6.9 \pm 0.3) \times 10^{-3}$
	40E		0.08		$(3.2 \pm 0.5) \times 10^{-2}$
	75A		2.0		$(6.3 \pm 0.05) \times 10^{-4}$
	50A		2.0		$(4.3 \pm 0.03) \times 10^{-3}$
	25A		2.0		$(1.28 \pm 0.02) \times 10^{-2}$
c-BuCar–OBs (7)	60E	2.0		$(7.89 \pm 0.1) \times 10^{-5}$	
	40E	0.08		$(6.5 \pm 0.2) \times 10^{-4}$	
	75A	2.0		$(2.78 \pm 0.06) \times 10^{-5}$	
	50A	2.0		$(1.04 \pm 0.01) \times 10^{-4}$	
	25A	2.0		$(2.43 \pm 0.08) \times 10^{-4}$	
c-C$_4$H$_7$–OBs (8)	90E		3.0		$(1.90 \pm 0.02) \times 10^{-5}$
	80E		2.0		$(8.4 \pm 0.1) \times 10^{-5}$
	70E		2.0		$(2.30 \pm 0.05) \times 10^{-4}$
	60E		2.0		$(6.8 \pm 0.2) \times 10^{-4}$
	50E		1.0		$(1.5 \pm 0.07) \times 10^{-3}$
	40E		0.08		$(7.2 \pm 0.4) \times 10^{-3}$
	75A		2.0		$(9.80 \pm 0.03) \times 10^{-5}$
	50A		2.0		$(6.0 \pm 0.2) \times 10^{-4}$
	25A		2.0		$(2.12 \pm 0.02) \times 10^{-3}$
	0A		2.0		$(6.3 \pm 0.1) \times 10^{-3}$
pin–OBs (9)	60E		0.6		$(4.31 \pm 0.05) \times 10^{-5}$
	50E		0.25		$(9.9 \pm 0.3) \times 10^{-5}$
	40E		0.07		$(4.3 \pm 0.2) \times 10^{-4}$
	75A		2.0		$(1.40 \pm 0.01) \times 10^{-5}$
	50A		2.0		$(7.98 \pm 0.05) \times 10^{-5}$
	25A		2.0		$(2.97 \pm 0.02) \times 10^{-4}$
c-C$_5$H$_9$–OTs (10)	90E		2.0		$(1.10 \pm 0.02) \times 10^{-5}$
	70E		2.0		$(5.47 \pm 0.05) \times 10^{-5}$
	50E		0.75		$(2.10 \pm 0.02) \times 10^{-4}$
	40E		0.08		$(8.0 \pm 0.2) \times 10^{-4}$
	75A		2.0		$(1.93 \pm 0.03) \times 10^{-5}$

Table I (Continued)

compd[a]	solvent[b]	concn, 10^2 M		k,[c] s^{-1}	
		45 °C	25 °C	45 °C	25 °C
c-C$_6$H$_{11}$-OTs (11)	25A		2.0		$(2.93 \pm 0.03) \times 10^{-4}$
	90E		2.0		$(2.8 \pm 0.1) \times 10^{-7}$
	70E		1.0		$(1.86 \pm 0.05) \times 10^{-6}$
	50E		0.6		$(7.3 ● 0.08) \times 10^{-6}$
	40E		0.07		$(2.8 \pm 0.05) \times 10^{-5}$
	75A		2.0		$(8.22 \pm 0.03) \times 10^{-7}$
2-Pr-OTs (12)	25A		2.0		$(1.45 \pm 0.02) \times 10^{-5}$
	90E		2.0		$(1.28 ● 0.03) \times 10^{-6}$
	70E		2.0		$(4.53 \pm 0.05) \times 10^{-6}$
	60E		1.0		$(8.47 \pm 0.05) \times 10^{-6}$
	40E		0.1		$(4.5 \pm 0.2) \times 10^{-5}$
	75A		2.0		$(8.33 \pm 0.2) \times 10^{-7}$
	50A		2.0		$(3.0 \pm 0.2) \times 10^{-6}$
	25A		2.0		$(9.44 \pm 0.3) \times 10^{-6}$
c-PeCar-OBs (13)	60E	1.5		$(3.67 \pm 0.02) \times 10^{-6}$	
	50E	0.75		$(5.6 \pm 0.2) \times 10^{-6}$	
	40E	0.08		$(1.4 \pm 0.1) \times 10^{-5}$	
	75A	1.2		$(1.37 ● 0.03) \times 10^{-6}$	
	50A	1.2		$(5.22 \pm 0.01) \times 10^{-6}$	
	25A	1.2		$(1.59 \pm 0.01) \times 10^{-5}$	

[a] Ada = adamantyl, c-PrCar = cyclopropylcarbinyl, c-BuCar = cyclobutylcarbinyl, pin = pinacolyl, Pr = propyl, c-PeCar = cyclopentylcarbinyl. [b] Per cent by volume. For example, 90E means 90 volumes of ethanol plus 10 volumes of water, both at 25 °C before mixing; 75A means 75 volumes of acetic acid plus 25 volumes of formic acid, both at 25 °C before mixing. [c] Errors reported as one standard deviation from the mean. [d] At 30 °C. [e] At 75 °C. [f] At 55 °C. [g] At 20 °C.

mY equation of Winstein and Grunwald[13] are useful tools for evaluating the mechanism of a solvolysis reaction. Accordingly, we have collected in Table III the values of m_{EW}, m_{AF}, and $[k_{EW}/k_{AcOH}]_Y$ for the arenesulfonates selected for the dispersion analysis carried out in this study. As can be seen, the m values for cyclobutyl brosylate,[14] *exo*-2-norbornyl tosylate, and the cyclopropylcarbinyl arenesulfonates are quite similar, a result which indicates a similar delocalization of charge in the transition states of these four compounds. The most interesting feature of the data in Table III, however, is the magnitudes of the $[k_{EW}/k_{AcOH}]_Y$ ratios observed for the solvolyses of compounds 5-8. They are all similar to that of neophyl tosylate. Since the neophyl system is generally accepted as a good model for k_Δ solvolysis,[5] this result supports the previous arguments that, in the solvent series investigated, nucleophilic solvent assistance is not significant in the solvolyses of compounds 5-8.

Statistical Analyses of Rate Data Correlations by Eq 1. To evaluate the validity of the E-line, A-line dispersions observed in plots of log $k_t(Y)$ vs. log k_t(neophyl-OTs), we expanded eq 1 to include a solvent series (E or A) classification variable. Then, to test the null hypothesis that the E or A variable was not significant, we processed the data of Table II by the SAS[16a] GLM procedure using the class-level statement option.[16b] As a test of the significance of the solvent series classification (E or A), we used the F statistic and a significance level of $\alpha = 0.05$. Thus for significance probabilities (PR > F)

less than 0.05 (the 5% significance level), we rejected the null hypothesis that the solvent series classification was not significant. Conversely, for significance probabilities greater than 0.05, we accepted the null hypothesis as true.

As can be readily seen from Table IV, the significance probability values for compounds 5-13 are sufficiently small to reject the hypothesis that the E or A classification is not significant. On the other hand, the significance probability values for compounds 2-4 are sufficiently large to accept the null hypothesis as true.

This result gives strong support to the contention that correlations of rate data for compounds 5-8 by use of eq 1 yield E-line, A-line dispersions, in sharp contrast to the simple linear relationships observed for the same correlations of rate data for compounds 2-4. Furthermore, the results of the statistical analysis suggest that an interesting relationship may exist between the solvolysis mechanisms assigned to compounds 5-14 listed in Table IV and their observed E-line, A-line dispersion patterns.

Solvolytic Mechanism and Dispersion Pattern. In Table V we have listed the compounds investigated in this solvolysis study, their assigned mechanisms, and the E-line, A-line dispersion patterns produced by eq 1 correlations of their solvolysis rates. It is evident from this table that the choice of model compounds is broad, covering a wide variety of solvolysis mechanisms. For example, listed are primary and secondary substrates thought to solvolyze by (1) k_s,[17] (2) k_Δ,[17] and (3) competing k_s-k_Δ processes.[17,18] Also listed are 2-adamantyl[19] and pinacolyl[20] tosylates which are currently contending for acceptance as k_c models for comparison with solvolyses of primary and secondary arenesulfonates.

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(14) Cyclobutyl brosylate is a substrate whose solvolytic transition state may well be stabilized by σ conjugation.[2d,15]

(15) (a) Wiberg, K. B. *Tetrahedron*, **1968**, *24*, 1083. (b) Wiberg, K. B.; Szeimies, G. *J. Am. Chem. Soc.* **1970**, *92*, 571. (c) Majerski, Z.; Schleyer, P. v. R. *Ibid.* **1971**, *93*, 665. (d) Olah, G. A.; Jewell, C. L.; Kelly, D. P.; Porter, R. D. *Ibid.* **1972**, *94*, 146. (e) Olah, G. A.; Berrier, A. L.; Arvanaghi, M.; Surya Prakash, G. K. *Ibid.* **1981**, *103*, 1122.

(16) (a) Statistical Analyses System. (b) For details of this procedure, see: "SAS User's Guide"; Helvig, J. T., Council, K. A., Eds.; SAS Institute Inc.: Cary, NC, 1979, pp 237-263.

(17) For a review, see: Lowrey, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; Chapters 4 and 5.

(18) Schadt, F. L; Lancelot, C. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 228 and references listed therein.

(19) For leading references, see: Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466.

(20) For leading references, see: Harris, J. M.; Mount, D. L.; Smith, M. R.; Neal, W. C., Jr.; Dukes, M. D.; Raber, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 8147.

Table II. Solvolysis Rates (-log k_t)[a] for Selected Substrates in E[b] and A[c] Solvent Series

compd	solvent												
	100E	90E	80E	70E	60E	50E	40E	100A	75A	65A	50A	25A	0A
neophyl-OTs[d] (1)	6.90[e]	6.30[f]	5.90[f]	5.50[f]	5.29[g]	5.05[h]	4.48[g]	6.30[e]	5.24[g]	4.97[g]	4.66[g]	4.26[g]	3.89[j]
neophyl-OTs[j] (1)	8.12[k]	7.45[f]	7.10[l]	6.70[l]	6.49[g]	6.23[g]	5.72[g]	7.60[e]	6.40[m]	6.08[g]	5.87[g]	5.32[m]	4.94[n]
2-ada-OTs[j,o] (2)	9.37	8.19	7.62	7.15	6.70	6.33	5.65[g]	8.23	6.70[m]		6.00[m]	5.28[m]	4.58
neopentyl-OTs[d] (3)	9.18[f]	8.65[f]	8.25[f]	7.8[f]	7.60[m]	7.30[m]	6.92[g]	8.70[f]	7.68[g]		7.11[g]	6.60[m]	6.37[f]
c-C$_8$H$_{15}$-OTs[j] (4)	5.37[p]	4.51[g]	3.98[p]	3.59[g]	3.24[q]	2.92[g]	2.19[g]	4.63[p]	3.28[g]		2.52[g]	1.94[g]	1.40[g]
c-PrCar-OPms[j] (5a)	5.10[r]	4.15[r]	3.60[r]	3.07[g]	2.55[g]	2.22[g]		4.48[r]	3.14[g]	2.81[g]	2.36[g]	1.90[t]	1.37[r]
c-PrCar-OTs[g] (5b)	4.49[t]	3.50[u]	2.94[t]	2.46[g]	1.96[g]	1.60[g]		3.89[t]	2.54[g]	2.19[g]	1.76[g]	1.34[g]	0.50[v]
exo-2-norbornyl-OTs[j] (6)	5.35[w]	4.15[g]	3.64[w]	3.18[g]	2.73[g]	2.16[g]	1.5[g]	4.63[w]	3.20[g]		2.35[g]	1.89[g]	1.29[w]
c-BuCar-OBs[d] (7)	5.89[h]	5.19[h]	4.72[h]	4.35[h]	4.10[g]	3.82[h]	3.18[g]	5.47[h]	4.56[g]		3.98[g]	3.61[g]	3.20[h]
c-C$_4$H-OBs[j] (8)	5.85[x]	4.72[g]	4.08[g]	3.63[g]	3.17[g]	2.82[g]	2.14[g]	5.30[x]	4.00[g]		3.22[g]	2.67[g]	2.20[g]
pin-OBs[j] (9)	6.68[y]	5.71[z]	5.20[z]	4.74[z]	4.37[g]	4.00[g]	3.37[g]	6.16[aa]	4.85[g]		4.10[g]	3.53[g]	3.07[aa]
c-C$_5$H$_9$-OTs[j] (10)	5.54[bb]	4.96[g]	4.52[bb]	4.26[g]	3.95[bb]	3.68[g]	3.10[g]	5.76[bb]	4.71[g]		3.92[bb]	3.53[g]	3.12[bb]
c-C$_6$H$_{11}$-OTs[j] (11)	7.37[bb]	6.55[g]	6.04[bb]	5.73[g]	5.41[bb]	5.14[g]	4.55[g]	7.52[bb]	6.08[g]		5.32[bb]	4.84[g]	4.41[bb]
2-Pr-OTs[j] (12)	6.41[aa]	5.89[g]	5.53[aa]	5.34[g]	5.07[g]	4.83[aa]	4.35[g]	7.11[aa]	6.08[g]		5.52[g]	5.02[g]	4.62[aa]
c-PeCar-OBs[d] (13)	6.68[h]	6.25[h]	5.95[h]	5.68[h]	5.44[g]	5.25[g]	4.84[g]	6.85[h]	5.86[g]		5.28[g]	4.80[g]	4.46[h]
2-phenyl-1-Pr-OTs[j] (14)		7.75[cc]	7.54[cc]	7.37[cc]	7.05[cc]			8.17[dd]					5.95[dd]

[a] In s^{-1}. [b] E series = per cent by volume aqueous ethanol mixtures. [c] A series = per cent by volume acetic acid–formic acid mixtures. [d] At 45 °C. [e] Calculated from data at higher temperatures contained in ref 4a. [f] Calculated from data at higher temperatures contained in ref 1e. [g] From data in Table I. [h] Reference 1f. [i] Calculated from data at higher temperatures contained in ref 3a. [j] At 25 °C. [k] Calculated from data at higher temperatures contained in ref 3a and 5a. [l] Calculated from data at higher temperatures contained in ref 1e and 5a. [m] Calculated from data at higher temperatures contained in Table I. [n] Reference 3a. [o] Reference 12b. [p] Calculated from data at higher temperatures contained in ref 22. [q] Reference 22. [r] Reference 1d. [s] At 20 °C. [t] Reference 1a. [u] Reference 1b. [v] Obtained from a plot of log k_t(c-PrCar–OPms) vs. log k_t(c-PrCar–OTs) in 11 solvents. [w] Taken from the data collected in Table II of ref 23. [x] Calculated from data at higher temperatures contained in ref 10. [y] Obtained from a plot of log k_t vs. Y for E series solvents. [z] Taken from data collected in Table II of ref 20. [aa] Taken from data collected in Table III of ref 21. [bb] Calculated from data at higher temperatures contained in ref 24. [cc] Taken from data collected in Table I of ref 7. [dd] Calculated from data at higher temperatures contained in ref 25.

Table III. Summary of Solvent Parameters[a] Derived from the mY Equation[b]

compd	m_{EW}[c]	m_{AF}[c]	$[k_{EW}/k_{AcOH}]Y$[d]
neophyl-OTs (1)	0.52 ± 0.01	0.71 ± 0.02	0.55
2-ada-OTs (2)	0.82 ± 0.02	0.96 ± 0.03	0.17
neopentyl-OTs[e] (3)	0.52 ± 0.02	0.64 ± 0.02	0.46
c-C$_8$H$_{15}$-OTs (4)	0.67 ± 0.01	0.86 ± 0.01	0.34
c-PrCar-OPms (5a)	0.79 ± 0.02	0.83 ± 0.02	0.44
c-PrCar-OTs[f] (5b)	0.79 ± 0.01	0.88 ± 0.05	0.49
exo-2-norbornyl-OTs (6)	0.84 ± 0.01	0.89 ± 0.03	0.42
c-BuCar-OBs[e] (7)	0.57 ± 0.01	0.61 ± 0.01	0.63
c-C$_4$H$_7$-OBs (8)	0.83 ± 0.02	0.84 ± 0.01	0.64
pin-OBs (9)	0.73 ± 0.01	0.83 ± 0.01	0.59
c-C$_5$H$_9$-OTs (10)	0.51 ± 0.01	0.72 ± 0.02	2.43
c-C$_6$H$_{11}$-OTs (11)	0.61 ± 0.01	0.84 ± 0.04	2.61
2-Pr-OTs (12)	0.43 ± 0.01	0.67 ± 0.01	7.18
c-PeCar-OBs[e] (13)	0.40 ± 0.01	0.65 ± 0.01	1.92
2-phenyl-1-Pr-OTs (14)	0.36 ± 0.05	0.55[f]	1.0

[a] Calculated from rate data listed in Table II at 25 °C by the method of least squares. [b] Y values used were taken from Table 8–14 of ref 12a and Table I of ref 12b. [c] Errors reported as standard error of the regression coefficient. [d] Values of k_{EW} were calculated from the regression equation. [e] Calculated from rate data listed in Table II at 45 °C. [f] Calculated from rate data listed in Table II at 20 °C. [g] Estimated from the rate data for acetolysis and formolysis.

The most interesting feature of Table V, however, is the apparent relationship between the observed E-line, A-line

dispersion patterns and mechanistic assignment. Thus for those primary and secondary compounds whose solvolyses may well involve neighboring-group assistance by σ conjugation (5–8), correlations using eq 1 yield an E-line, A-line dispersion characterized by a diverging pattern (i.e., the difference between the correlation lines for the two solvent series E and A increases with increasing solvent ionizing power). On the other hand, correlations for those secondary arenesulfonates whose solvolyses are thought to be assisted nucleophilically by the solvent (10–12) yield E-line, A-line dispersions characterized by a parallel pattern (i.e., the difference between the correlation lines for the two solvent series remains invariant with increasing solvent ionizing power). And finally, for those compounds assigned a competing k_s–k_Δ mechanism (13 and 14), eq 1 correlations yield E-line, A-line dispersions characterized by a converging pattern (i.e., the difference between the correlation lines for the E and A solvents decreases with increasing solvent ionizing power).

The dispersion pattern observed for the k_s compounds (10–12) is understandable in terms of the extended Winstein–Grunwald equation[12b] [log $(k/k_0) = lN + mY$] which explicitly considers both the ionizing power (Y) and the nucleophilicity (N) of the solvent. In the formulation of Schleyer and co-workers,[12b] the Y values are designated Y_{OTs} and are based on the solvolyses of 2-adamantyl tosylate. The N values, in turn, are based on the solvolyses of methyl tosylate. In our eq 1 correlations, the log k_t (neophyl–OTs) values are proportional to the Y_{OTs} values since a plot of logarithms of solvolysis rates for 2-adamantyl tosylate vs. neophyl tosylate is linear (see Table IV). Furthermore, since the Schleyer N values[12b] change little with change in solvent composition in both ethanol/water and acetic acid/formic acid mixtures, the contribution of the N term in solvent effect correlations would

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Table IV. Results of Correlations and Statistical Analyses

compd	E-line, A-line disperse pattern[a]	correlations			statistical analyses	
		b_{EW}[b]	b_{AF}[c]	b[d]	F value[e]	$PR > F$[f]
2-ada-OTs (2)	none	1.56 ± 0.04	1.35 ± 0.04	1.43 ± 0.04	0.13	0.72
neopentyl-OTs (3)	none	0.97 ± 0.03	0.99 ± 0.03	0.96 ± 0.02	4.43	0.07
c-C_8H_{15}-OTs (4)	none	1.31 ± 0.02	1.21 ± 0.03	1.24 ± 0.02	3.15	0.11
c-PrCar-OPms (5a)	D[g]	1.54 ± 0.05	1.17 ± 0.04	1.15 ± 0.09	17.92	0.002
c-PrCar-OTs (5b)	D[g]	1.52 ± 0.04	1.23 ± 0.07	1.18 ± 0.09	20.84	0.001
exo-2-norbornyl-OTs (6)	D[g]	1.60 ± 0.05	1.24 ± 0.05	1.28 ± 0.10	20.27	0.001
c-BuCar-OBs (7)	D[g]	1.11 ± 0.01	0.94 ± 0.02	0.91 ± 0.08	76.59	0.0001
c-C_4H_7-OBs (8)	D[g]	1.55 ± 0.04	1.17 ± 0.03	1.17 ± 0.13	39.27	0.0001
pin-OBs (9)	D[g]	1.38 ± 0.02	1.17 ± 0.03	1.15 ± 0.08	46.49	0.0001
c-C_5H_9-OTs (10)	P[h]	1.01 ± 0.03	1.00 ± 0.05	0.84 ± 0.11	201.29	0.0001
c-C_6H_{11}-OTs (11)	P[h]	1.16 ● 0.03	1.17 ± 0.04	1.00 ± 0.12	310.74	0.0001
2-Pr-OTs (12)	P[h]	0.85 ● 0.03	0.93 ± 0.02	0.65 ± 0.16	608.21	0.0001
c-PeCar-OBs (13)	C[i]	0.77 ± 0.02	1.00 ± 0.02	0.78 ± 0.07	30.01	0.0004
2-phenyl-1-Pr-OTs (14)	C[i]	0.67 ± 0.12	0.83[j]	0.78 ● 0.06		

[a] Based on visual inspection of computer plots of log $k_t(Y)$ vs. log k_t(neophyl-OTs). [b] Calculated slope values for rate data correlations by eq 1 with E data only. [c] Calculated slope values for rate data correlations by eq 1 with A data only. [d] Calculated slope values for rate data correlations by eq 1 with both E and A data. [e] Analysis of variance test; see ref 16b for details as to how calculated. [f] Significance probability. [g] D = diverging E and A lines with increasing ionizing power. [h] P = parallel E and A lines with increasing ionizing power. [i] C = converging E and A lines with increasing ionizing power. [j] Estimated from a two point data set.

Table V. Summary of Mechanistic Assignments and Observed E-Line, A-Line Dispersion Patterns

compd	mechanistic assignment	E-line, A-line disperse pattern
neophyl-OTs (1)	k_Δ (bridging)[a]	
2-ada-OTs (2)	k_c[b]	none
neopentyl-OTs (3)	k_Δ (bridging)[c],[D]	none
c-C_8H_{16}-OTs (4)	k_Δ (bridging)[e]	none
c-PrCar-OPms (5a)	k_Δ[f],[g]	diverging
c-PrCar-OTs (5b)	k_Δ[f]	diverging
exo-2-norbornyl-OTs (6)	k_Δ[h],[i]	diverging
c-BuCar-OBs (7)	k_Δ[j]	diverging
c-C_4H-OBs (8)	k_Δ[k],[l]	diverging
pin-OBs (9)	$(?)$[m]	diverging
c-C_5H_9-OTs (10)	k_s[b]	parallel
c-C_6H_{11}-OTs (11)	k_s[b]	parallel
2-Pr-OTs (12)	k_s[b]	parallel
c-PeCar-OBs (13)	(k_s-k_Δ)[n],[o]	converging
2-phenyl-1-Pr-OTs (14)	(k_s-k_Δ)[p],[q]	converging

[a] For leading references see ref 5c. [b] Reference 19. [c] For leading references see: Shiner, V. J., Jr.; Tai, J. *J. Am. Chem. Soc.* **1981**, *103*, 436. [d] Also see ref 3c. [e] For leading references see ref 26. [f] Reference 1d. [g] Also see ref 1c. [h] Reference 6. [i] Also see ref 7. [j] Reference 27. [k] Reference 10. [l] Also see ref 2d. [m] Reference 20. [n] Reference 27. [o] Reference 1f. [p] Reference 28. [q] Reference 7.

be proportional to ΔN, the difference in nucleophilicity of the two solvent systems. This means that an eq 1 correlation of a k_s substrate would yield separate E and A correlation lines differing only by a factor proportional to $l\Delta N$ where l represents the substrate's sensitivity to solvent nucleophilicity. The result would be a dispersion of the points into two parallel lines, as observed, whose separation distance would depend upon the substrate's l value.

An explanation for the dispersion pattern observed for the k_Δ substrates (5-8) is more difficult to formulate. However, some insight into the reason for the dispersion can be gained by an analysis of the relationship between transition state structure and the involvement of solvent at the transition state. Structures I and II (Figure 1) are illustrative of σ conjugated and bridging transition states, respectively. Traylor[2a] has proposed that in σ conjugation (hyperconjugation) there is little nuclear motion of G, as
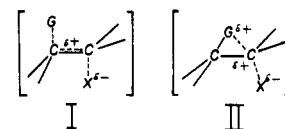

Figure 1.

in I, while in bridging there is much, as in II. Using this distinction between the two delocalization phenomena, we note that the transition state for solvolysis of neophyl tosylate should be similar in structure to II. This is so because it is generally recognized[5] that the neighboring phenyl group plays the role of an intramolecular nucleophile displacing the leaving group. On the other hand, the transition states for solvolyses of the k_Δ compounds listed in Table V (5-8) should be similar in structure to I. This is so because (1) the geometry of each of their proposed cations is favorable for σ conjugation of a neighboring C-C σ bond with the incipient vacant p orbital at the cationic center,[1d,2d,6,27] and (2) the neighboring C-C σ bond present in each case very likely posesses the excess p character which leads to the increased hyperconjugative stabilization called exhalted hyperconjugation.[29-31]

The solvation consequences of the structural differences between transition states I and II is understandable in terms of the empirical constants derived from recent studies of solvent effects upon relative rates.[32,33] For example, in II, backside solvation is, to a large measure, blocked by G, and, therefore, solvolyses of substrates proceeding by this transition state should show little sensitivity to what Parker[32] and Swain[33] call the cation solvating power of the solvent. Conversely, in I, backside cation solvation should be more favorable, and, hence, substrates solvolyzing via this transition state should show, in addition to their strong response to anion solvating power, some small but significant response to the cation

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solvating power of the solvent. This type of situation is what we encounter in the eq 1 correlations of the listed k_Δ compounds. Since water is a far better cation solvator than formic acid,[33] the cation-solvating power of the medium should be increased more markedly by increasing water content in the ethanol/water solvents than by increasing formic acid content in the carboxylic acid solvents. As a result, the points for the aqueous alcohol solvents would fall, as we observed, on a correlation line different from that of the points for the carboxylic acid solvents. More importantly, the slope value for the aqueous alcohol correlation line would be higher, as we observed, than that for the carboxylic acid correlation line. We, therefore, argue that the dispersion of data reported for the eq 1 correlations of compounds 5–8 can be attributed, at least in part, to the inadequacy of the ionizing power scale based on neophyl tosylate to account for cation solvation effects.

Conclusions

There are at least three important conclusions that can be drawn from the noted relationship between dispersion pattern and mechanistic assignment. They are as follows: (1) The fact that the relationship holds for 13 diverse primary and secondary substrates, spanning a wide range of solvolytic behavior, argues against the possibility that this relationship is merely fortuitous. (2) The fact that the relationship shows a significant different response to solvent effect(s) by compounds 5–8 from that by both k_s and k_s–k_Δ substrates argues against nucleophilic solvent assistance as an explanation for the dispersions observed for compounds 5–8. (3) The fact that the relationship shows a significantly different response to solvent effect(s) by compounds 5–8 from that by k_Δ (bridging) substrates provides additional support for our proposal that delocalization of charge by exhalted hyperconjugation[2] can be differentiated from that by bridging by use of eq 1 correlations.

It is also of interest to note that the data in Table V show that the response of pinacolyl brosylate to the examined solvent effect(s) is very similar to that of compounds 5–8. While, on the basis of this observation, it is tempting to assign to the solvolyses of pinacolyl brosylate a k_Δ mechanism,[34] our data are not sufficiently well developed to permit such a definitive assignment of mechanism.

Experimental Section

Preparation of Arenesulfonates. All arenesulfonates were prepared by published procedure.[1e] In a typical run, the appropriate arenesulfonyl chloride (35 mmol) was added all at once to a hand stirred solution of the alcohol (30 mmol) in 40 mL of dry pyridine (spectrophotometric grade, Aldrich Chemical Co.) cooled to 0 °C. After standing 48 h at about 5 °C,[35] the mixture was carefully hydrolyzed by the slow addition of 20 mL of cold water (reaction temperature maintained between 0 and 5 °C) followed by the addition of sufficient cold, dilute HCl (reaction temperature maintained between 5 and 10 °C) to acidify the mixture and separate out the ester. Neophyl, 2-adamantyl, neopentyl, *exo*-2-norbornyl, cyclopentyl, and cyclohexyl tosylates, cyclopropylcarbinyl pentamethylbenzenesulfonate, and cyclobutylcarbinyl, cyclobutyl, pinacolyl, and cyclopentylcarbinyl brosylates separated as solids. Each was then purified by washing three times with 50-mL portions of cold, dilute HCl and three times with 50-mL portions of cold water, followed by air drying.

Crystallization from pentane–benzene gave the purified arenesulfonates, with melting points in agreement with literature values.[1d,4a,27,36–42]

Cyclooctyl, cyclopropylcarbinyl, and 2-propyl tosylates separated as oils.[1c,43,44] Therefore, each of their resultant acidified mixtures was extracted twice with 40-mL portions of methylene chloride. The combined extracts for each ester were then washed two times with 50-mL portions of cold, dilute HCl, twice with 40-mL portions of cold water, and twice with 20-mL portions of 10% aqueous NaHCO₃ and dried over anhydrous Na₂SO₄, and most of the solvent was removed by rotovaporization. Cyclooctyl tosylate was further purified by separation as an oil[43] from petroleum ether (bp 50–70 °C, 2.5 mL of solvent per g of oil) at ice bath temperature. The solvent was then removed from the precipitated ester by decantation, followed by rotovaporization at reduced pressure. Kinetic analysis revealed that the oil was 99% cyclooctyl tosylate.

Cyclopropylcarbinyl tosylate was purified as above. Kinetic analysis revealed that the oil was 95% cyclopropylcarbinyl tosylate. 2-Propyl tosylate was purified by separation (as a solid) from a 20:1 mixture of pentane–ethyl acetate at dry ice–acetone temperature. Filtration using a chilled Hirsch funnel yielded a powdery solid that melted just below room temperature. Kinetic analysis revealed that the 2-propyl tosylate was at least 99% pure.

Solvents were purified as previously described.[1d]

Rate Measurements. The rates of solvolysis were followed titrimetically. In a typical kinetic run, the requisite amount of ester was accurately weighed into a 25-mL volumetric flask and then sufficient solvent was added rapidly to give a 25-mL reaction solution volume.[45] Reaction time commenced with the addition of the solvent. The solvent used for each kinetic run and the flask containing the ester were thermostated in a constant temperature bath held at ±0.05 °C at least 5 min prior to a run. At appropriate times, 2-mL aliquots were analyzed for liberated arenesulfonic acid.[46] The titrating solutions were as follows: for acetic acid–formic acid solvents, 0.020 N sodium acetate in acetic acid and for the aqueous ethanol solvents, 0.016 N sodium methoxide in methanol. The indicators used were as follows: for acetic acid–formic acid solvents, bromophenol blue (in acetic acid), 2–3 drops, and for aqueous ethanol solvents, bromothymol blue (in water), 2 drops.

Treatment of Kinetic Data. The slope values recorded in Tables III and IV were obtained by regression analyses of log $k_t(Y)$ vs. Winstein–Grunwald Y values and log k_t(neophyl–OTs) values, respectively. The statistical parameters listed in Table IV were obtained by processing the kinetic data by the SAS[16a] GLM procedure using the class-level statement option.[16b]

Registry No. 1, 21816-03-5; 2, 25139-43-9; 3, 2346-07-8; 4, 6597-09-7; 5a, 70561-86-3; 5b, 1015-45-8; 6, 959-42-2; 7, 51108-24-8; 8, 27852-78-4; 9, 26325-42-8; 10, 3558-06-3; 11, 953-91-3; 12, 2307-69-9; 13, 38806-24-5; 14, 23430-41-3.

(34) On the basis of another solvent effect study, Bentley[19] has recently proposed that the solvolyses of pinacolyl tosylate are either k_s or k_Δ.

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(45) For reactions whose half-lives were greater than 60 h, rate measurements were accomplished by the ampule technique.[1f]

(46) For reactions whose half-lives were less than 10 min, the aliquots taken from aqueous ethanol mixtures were quenched with 3 mL of cold ethanol before titration, while those taken from acetic acid–formic acid mixtures were quenched with 3 mL of cold acetic acid before titration. Also, for reactions whose concentrations were less than 1×10^{-2} M, 3-mL aliquots were titrated; for those whose concentrations were less than 1×10^{-3} M, 5-mL aliquots were titrated.