The SN2-SN1 Spectrum. 2. Quantitative Treatments of Nucleophilic Solvent Assistance. A Scale of Solvent Nucleophilicities[1]

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Abstract: The Winstein-Grunwald equation, $\log (k/k_0) = lN + mY$, for correlating solvolysis rate constants is evaluated for tosylates. A solvent nucleophilicity scale (N) is defined from rate data for methyl tosylate: $N = \log (k/k_0)_{CH_3OTs} - 0.3Y$; the term $0.3Y$ corrects for the sensitivity of methyl tosylate solvolyses to solvent ionizing power (Y). Values of Y based on 2-adamantyl tosylate, $Y_{2\text{-AdOTs}}$, are employed instead of those for *tert*-butyl chloride in order to retain the same leaving group and eliminate complications from ion pairing effects. The $lN + mY$ equation give significantly improved correlations over the simple mY equation, e.g., for ethyl, 2-propyl, and cyclohexyl tosylates in solvents varying in nucleophilicity and ionizing power from ethanol to trifluoroacetic acid. A three-parameter equation, $\log (k/k_0) = (1 - Q) \log (k/k_0)_{CH_3CTs} + Q \log (k/k_0)_{2\text{-AdOTs}}$ also correlates solvolysis rate constants for substrates subject to varying amounts of nucleophilic (but not anchimeric) assistance. Q is an adjustable blending parameter which measures the substrate's sensitivity to solvent nucleophilicity relative to SN2 (methyl tosylate) and SN1 (2-adamantyl tosylate) models. The high accuracy of correlations by both the four-parameter Winstein-Grunwald equation and the Q equation realizes a long-held goal of physical organic chemistry to correlate and predict solvolysis rate constants in different solvents to within a factor of 2-3. The observed interdependence of Q, m, and l for simple primary and secondary solvolyses between the methyl and 2-adamantyl extremes is interpreted in terms of a spectrum of nucleophilic solvation in the first transition state. In the part of the spectrum where there is evidence for a reaction intermediate, as well as for nucleophilic solvent assistance, the mechanism is designated as SN2 (intermediate), to signify that the five-coordinate species usually regarded as a transition state may in some cases be an intermediate (a nucleophilically solvated ion pair). Solvolysis of 2-adamantyl tosylate is used as a model for estimates of nucleophilic solvent assistance (k_s/k_c) in the solvolyses of the other secondary substrates (Table IV). The calculated k_s/k_c ratios, which correlate with α-deuterium isotope effects, and other evidence suggests that it is not necessary to postulate hidden internal ion pair return of appreciable magnitude to describe secondary solvolyses.

In 1948, Grunwald and Winstein proposed a scale of solvent ionizing power, based on *tert*-butyl chloride (eq 1),[3a,4] to correlate SN1 or k_c

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

solvolyses.[5,6] Later they provided a formal expression to account for nucleophilically solvent assisted (k_s) processes (eq 2),[3b,h] which leads to eq 3

$$d \log k = \left(\frac{\partial \log k}{\partial N}\right)_Y dN + \left(\frac{\partial \log k}{\partial Y}\right)_N dY \qquad (2)$$

$$\log (k/k_0) = lN + mY \qquad (3)$$

if the partial derivatives are constant and equal to l and m, respectively.[3h] Although comparisons of $(\partial \log k/\partial N)_Y$, measured by $[k_{ROH}/k_{RCO_2H}]_Y$, provided useful relative values of l,[3b,11] eq 3 was never explicitly evaluated, but was used implicitly as eq 1 when the lN term was considered either to make a negligible (k_c; $(\partial \log k/\partial N)_Y = 0$) or constant ($k_s$ solvolyses in solvents of similar nucleophilicities; $dN \cong 0$ contribution.[3h] Thus, even the SN2 solvolyses of methyl and primary substrates are correlated by eq 1 in solvents of similar nucleophilicities such as ethanol-water mixtures.[11]

Swain, Mosely, and Bown evaluated a similar four-parameter relationship (eq 4),[12]

$$\log (k/k_0) = c_1 d_1 + c_2 d_2 \qquad (4)$$

where d_1 and d_2 are measures of solvent nucleophilicity and electrophilicity, respectively, and c_1 and c_2 are measures of substrate's sensitivity to these solvent properties. The approach is essentially statistical since all four parameters are varied, in contrast to eq 3 in which only two, l and m, are adjustable. Although satisfactory correlation was achieved for a wide

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range of substrates and solvents, the treatment has been criticized on several grounds,[3h,13] some of which the authors acknowledge,[12] and the substrate factors c_1 and c_2 are of little mechanistic significance. A striking example is the indication by c_1 of an *increasing* sensitivity to solvent nucleophilicity in the series MeBr = EtBr < *i*-PrBr < 1-bromobicyclo[2.2.2]-octane < *t*-BuCl.[3h,13]

A promising correlation was introduced by Swain, Dittmer, and Kaiser[14] (eq 5), but has received little further attention.

$$\log (k/k_0)_A - \log (k/k_0)_{A^0} = ab \qquad (5)$$

In this equation, $(k/k_0)_A$ refers to the solvolysis rate constants for any organic chloride or bromide (A), and $(k/k_0)_{A^0}$ to the standard, methyl bromide (A^0). The rationale of this approach involves the cancellation of effects common to the substrate (A) and methyl (A^0) which solvolyses by an SN2 mechanism.[11,14] The factor a depends on the ability of the substrate to undergo heterolysis without nucleophilic solvent assistance (k_c),[6] and b is related to solvation properties such as acidity and dielectric constant. In contrast to c (eq 4), a values are mechanistically interpretable, increasing in the SN2-SN1 spectrum: MeBr (0.00, defined), EtBr (0.15), *n*-BuBr (0.18), *i*-PrBr (0.42), and *t*-BuCl (1.00, defined).

Several methods of correlating the bimolecular substitution reactions of various nucleophiles, usually in a standard solvent, have also been proposed.[15] As these reactions are dominated by effects of nucleophilicity, two parameter equations are satisfactory (i.e., in eq 2, $dY = 0$).

For correlation of solvolysis rate constants, we felt that the complete Winstein-Grunwald relation (eq 3) provided the most practical, generally applicable, and mechanistically significant approach.[16] Equation 3 has recently been used successfully to study the different responses to solvent properties of the anchimerically assisted (k_Δ) and anchimerically unassisted (k_s) processes in systems containing a neighboring

Table I. Summary of Solvolysis Data for 2-Adamantyl Tosylate and Methyl Tosylate. Y and N Values

Solvent vol %[a]	2-Adamantyl tosylate[b,c] $k \times 10^5$ s^{-1}; 25 °C	Methyl tosylate $k \times 10^5$, s^{-1}; 50 °C	2-Adamantyl tosylate scale		t-Butyl chloride scale	
			$Y_{2\text{-AdOTs}}$[d]	N_{OTs}[e]	Y[f]	N[e]
CH$_3$CH$_2$OH–H$_2$O						
100	0.000043	0.655[c,g]	−1.75	0.00	−2.03	0.09
90	0.00064	1.55[h]	−0.58	0.01	−0.75	0.05
80	0.0024	2.22[g]	0.00	0.00	0.00	0.00
70	0.0071	2.76[h]	0.47	−0.05	0.60	−0.09
60	0.020	3.48[h]	0.92	−0.08	1.12	−0.14
50	0.047	4.41,[g] 4.38[aa]	1.29	−0.09	1.66	−0.20
H$_2$O		13.8[j]			3.49	−0.26
CH$_3$OH–H$_2$O						
100	0.00029[i]	1.06[g]	−0.92	−0.04	−1.09	0.01
90		1.91[h]			−0.30	0.02
80		2.75[h]			0.38	−0.02
70		3.72[h]			0.96	−0.07
60		4.69[h]			1.49	−0.13
50		5.75[h]			1.97	−0.18
(CH$_3$)$_2$CHOH		0.414[k]			−2.73	0.09
(CH$_3$)$_2$CO–H$_2$O						
90		0.23[l]			−1.86	−0.43
80		0.44[l]			−0.67	−0.51
70		0.80[l]			0.13	−0.49
60	0.0111[m]	1.38[l]	0.66	−0.41	0.80	−0.45
50		2.14[l]			1.40	−0.44
Dioxane–H$_2$O						
90		0.13[n]			−2.03	−0.65
80		0.46[n]			−0.83	−0.43
70		0.85[n]			0.01	−0.42
60		1.45[n]			0.72	−0.41
50		2.34[n]			1.36	−0.39
CH$_3$CO$_2$H	0.00059	0.00632[c,o]	−0.61	−2.35	−1.64	−2.05
HCO$_2$H	2.65	0.083[c,o]	3.04	−2.35	2.05	−2.05
CF$_3$CO$_2$H	90	0.000143[c,p]	4.57	−5.56	1.84[q]	−4.74
FSO$_3$H		81.7[r]	~17[s]	~−4		
CF$_3$CH$_2$OH–H$_2$O[t]						
100	0.151[u]	0.0076[c,w]	1.80	−3.0 −3.8[v]	1.045[x]	−2.78
97	0.164[z]	0.0128[c,w]	1.83	−2.79	1.15[x]	−2.59
84.5	0.200[aa]	0.0823[c,w]	1.92	−2.01	1.35[u,x]	−1.83
70	0.243[z]	0.564[c,w]	2.00	−1.20	1.66[x]	−1.09
50	0.335[aa]	1.13[c,w]	2.14	−0.93	2.23[x]	−0.96
CF$_3$CH$_2$OH–CH$_3$CH$_2$OH						
80		0.083[bb]			0.41[bb]	−1.55
50		0.35[bb]			−0.59[bb]	−0.63
20		0.63[bb]			−1.52[bb]	−0.09
(CF$_3$)$_2$CHOH–H$_2$O[t]						
97	9.75[z]	0.00144[c]	3.61	−4.27	2.46[cc]	−3.93

[a] Volume percent of first named component except where stated otherwise. [b] Actual kinetic data is summarized in ref 11. [c] Calculated from data at other temperatures. [d] Calculated from log $(k/k_0)_{2\text{-AdOTs}}$ = $Y_{2\text{-AdOTs}}$; k_0 is the rate constant in 80% (vol) aqueous ethanol. [e] Calculated from rate constants of methyl tosylate at 50 °C, appropriate values of Y, and eq 8. [f] Reference 3c. [g] R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953). [h] Calculated from data for methyl benzenesulfonate (J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **34**, 931 (1956), and the average $(OTs/OSO_2Ph)_{CH_3}$ ratio, 0.66 ± 0.04, in aqueous and alcoholic solvents (EtOH, CH$_3$OH, H$_2$O, and 50 and 80% (vol) aqueous EtOH). [i] Calculated from a plot of log $k_{2\text{-AdOTs}}$ vs. $Y_{t\text{-BuCl}}$ for alcoholic and aqueous alcoholic solvents. [j] R. E. Robertson, *Can. J. Chem.*, **33**, 1536 (1955). [k] J. B. Hyne and R. E. Robertson, *ibid.*, **34**, 863 (1956). [l] Calculated from data for ethyl benzenesulfonate [E. Tommila and J. Jutila, *Acta Chem. Scand.*, **6**, 844 (1952)] and eq 9. [m] D. Lenoir, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 2138 (1974). [n] Calculated from data for ethyl benzenesulfonate, ref 50 and eq 9. [o] Reference 20. [p] I. Lazdins Reich, A. Diaz, and S. Winstein, *J. Am. Chem. Soc.*, **91**, 5635 (1969). [q] Reference 10c. [r] A. Diaz, I. Lazdins Reich, and S. Winstein, *ibid.*, **91**, 5637 (1969). [s] Approximated from a plot of log k_Δ (n-propyl tosylate) vs. $Y_{2\text{-AdOTs}}$ at 30 °C, ref p. [t] Wt % of first named component. [u] Calculated from an $mY_{t\text{-BuCl}}$ plot for aqueous TFE mixtures. [v] Extrapolated from methyl tosylate rate data at other TFE concentrations. [w] Reference 17d. [x] Reference 9a. [y] Calculated from eq 3 using m and l (0.36, 0.82) for ethyl tosylate, Y_{OTs} (TFE), and the rate constant for ethyl tosylate in TFE [D. S. Noyce and R. L. Castenson, *J. Am. Chem. Soc.*, **95**, 1247 (1973)]. This is probably inaccurate due to extrapolation errors, ref 17b. Compare with results for (CF$_3$)$_2$CHOH. [z] Table 11. [aa] D. J. Raber, unpublished results. [bb] D. A. da Roza, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **95**, 7003 (1973). [cc] Reference 9d.

group.[17] We have also used the three-parameter equation (6),

$$\log (k/k_0) = (1 - Q) \log (k/k_0)_{CH_3OTs} + Q \log (k/k_0)_{2\text{-AdOTs}} \quad (6)$$

which correlates solvolysis rate constants by comparison with two standard substrates: e.g., limiting SN1(2-adamantyl) and SN2(methyl) systems.[1] In this paper, we present a full discussion of eq 1, 3, and 6, and their application in testing proposed mechanisms of aliphatic nucleophilic substitution and elimination.[18]

Table II. Solvolysis Rate Constants for Alkyl Tosylates

Substrate	Solvent[a]	Temp, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Methyl tosylate	80% aqueous dioxane	75.15	$(3.86 \pm 0.03) \times 10^{-5}$	19.3	−23.8
		89.73	$(1.23 \pm 0.02) \times 10^{-4}$		
		50.00[b]	4.11×10^{-6}		
	90% aqueous dioxane	75.16	$(9.71 \pm 0.10) \times 10^{-6}$	17.6	−31.4
		89.67	$(2.79 \pm 0.02) \times 10^{-5}$		
		50.00[b]	1.25×10^{-6}		
	97% aqueous hexafluoroisopropanol	75.20	$(3.51 \pm 0.06) \times 10^{-7}$	28.1	−7.6
		89.22	$(2.07 \pm 0.13) \times 10^{-6}$		
		100.01	$(5.49 \pm 0.30) \times 10^{-6}$		
		50.00[b]	1.44×10^{-8}		
Ethyl tosylate	80% aqueous ethanol[c]	50.0[d-f]	$(9.38 \pm 0.15) \times 10^{-6}$		
	50% aqueous ethanol[c]	50.0[d-f]	$(2.18 \pm 0.01) \times 10^{-5}$		
	Ethanol	50.0[b,d-f]	$(2.33 \pm 0.14) \times 10^{-6}$		
	Methanol	50.0[d-f]	$(4.88 \pm 0.05) \times 10^{-6}$		
	Acetic Acid	50.0[b,e]	3.83×10^{-8}		
	Formic acid	50.0[b,e]	1.48×10^{-6}		
	Trifluoroacetic acid	50.0[b,g]	1.85×10^{-8}		
2-Adamantyl tosylate	70% aqueous Trifluoroethanol	49.77	$(6.19 \pm 0.15) \times 10^{-5}$	24.4	−2.4
		75.09	$(1.06 \pm 0.03) \times 10^{-3}$		
		25.00[b]	2.43×10^{-6}		
	97% aqueous Trifluoroethanol	49.83	$(3.62 \pm 0.05) \times 10^{-5}$	23.2	−7.1
		75.03	$(5.35 \pm 0.13) \times 10^{-4}$		
		25.00[b]	1.64×10^{-6}		
	97% aqueous Hexafluoroisopropanol	25.08	$(9.83 \pm 0.13) \times 10^{-5}$	17.9	−17.0
		49.81	$(1.07 \pm 0.02) \times 10^{-3}$		
		25.00[b]	9.75×10^{-5}		
2-Propyl tosylate	70% aqueous Trifluoroethanol	25.00[h]	3.8×10^{-6}		
	97% aqueous Trifluoroethanol	50.55[i]	$(1.20 \pm 0.02) \times 10^{-5}$	21.1	−16.1
		75.17[i]	$(1.31 \pm 0.01) \times 10^{-4}$		
		25.00[b,i]	6.66×10^{-7}		
		25.00[j,k]	6.96×10^{-7}		
	97% aqueous hexafluoroisopropanol	49.75	$(2.64 \pm 0.07) \times 10^{-5}$	21.3	−13.7
		75.27	$(3.24 \pm 0.05) \times 10^{-4}$		
		25.00[b]	1.55×10^{-6}		
Cyclohexyl tosylate	70% aqueous trifluoroethanol	25.00[h]	4.9×10^{-6}		
	97% aqueous trifluoroethanol	25.00[h]	1.4×10^{-6}		
	97% aqueous hexafluoroisopropanol	24.99	$(1.81 \pm 0.02) \times 10^{-5}$	20.5	−11.5
		49.76	$(2.79 \pm 0.18) \times 10^{-4}$		
		25.00[b]	1.81×10^{-5}		

[a] Weight percent of nonaqueous component unless otherwise noted. [b] Calculated from data at other temperatures. [c] Volume percent of nonaqueous component. [d] Average of two reported values. [e] Reference 3b. [f] R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953). [g] Table 1, footnote p. [h] Estimated rate constant for the brosylate (ref 25a) corrected to the tosylate by the (OBs/OTs) = 3.0, ref 11. [i] 97% (vol) aqueous trifluoroethanol, R. E. Hall, A. B. Thesis, Princeton University, 1970. [j] Corrected to 97% (wt) aqueous trifluoroethanol. [k] Less reliable value (6.4 × 10^{-7}) reported in ref 21a.

Results and Discussion

Evaluation of the Winstein–Grunwald Equation (3). Definition of N Constants. Peterson and Waller[19] have proposed several ways to evaluate the necessary solvent nucleophilicity constants, N. However, the most direct of these involves measurement of rates of displacement on tetramethylene halonium ions in liquid SO_2, a method not easily undertaken, and at present only applicable to carboxylic acid solvents. We have derived a scale of solvent nucleophilicity by rearrangement of eq 3 and solving for N (eq 7), using methyl tosylate to

$$N = [\log (k/k_0) - mY]/l \qquad (7)$$

provide appropriate data, k/k_0.[1] We define l equal to 1.00 for methyl solvolyses since they are the most sensitive of all simple alkyl tosylates to changes in solvent nucleophilicity.[3b,11,13,20] The sensitivity of methyl solvolyses to ionizing power is obtained from a solvent series in which Y varies but not N (eq 2, $dN = 0$). Since Peterson and Waller[19] have shown that acetic and formic acids are almost equally reactive toward halonium ions in liquid SO_2 and this reaction is nearly independent of

the ionizing power of these acids, it appears that they are almost equally nucleophilic. Thus, the m_{AF} ("apparent m" of Winstein[3b,11,13,20]) of 0.30 for methyl tosylate provides a reasonably good estimate of m for substitution into eq 7. Hence, nucleophilicity constants, N (Table I), were calculated using the following equation (8):

$$N = \log (k/k_0)_{CH_3OTs} - 0.3Y \qquad (8)$$

In the present study it was desirable to have a scale of solvent ionizing power derived from tosylate data, $Y_{2\text{-AdOTs}}$, because Y values based on the solvolyses of *tert*-butyl chloride generally produce dispersion in correlations applied to limiting (k_c) substrates having other leaving groups.[3g,i] Also, *tert*-butyl chloride behaves anomalously in certain fluorinated solvents because of ion pair partitioning effects.[9,10] For compounds containing sulfonate leaving groups,[3i] Winstein suggested p-methoxyneophyl tosylate, a k_Δ substrate, as a standard to measure ionizing power, uncomplicated by internal return. Unfortunately, data in the more highly ionizing media are not available, and we have chosen 2-adamantyl tosylate as the reference compound.[1,17,21] Although a secondary substrate,

Table III. Results of Various Correlations (25 °C)

| | | Equations | | | | | | | | | |
| | | $lN_{OTs} + mY_{2\text{-}AdOTs}$ (3) | | | | $mY_{2\text{-}AdOTs}$ (1) | | | Q (6) | | |
Tosylates	Solvents[a]	l	m	Correlation coeff	r^b	m	Correlation coeff	r^b	Q	Correlation coeff	r^b
Ethyl[c]	Std	0.89	0.40	0.998	0.10	0.14	0.244	0.80	0.12	0.998	0.07
	Std, TFA	0.83	0.41	0.996	0.11	−0.18	−0.344	0.89	0.16	0.996	0.09
2-Propyl	Std	0.49	0.62	0.993	0.17	0.48	0.838	0.45	0.48	0.993	0.13
	Std, TFA	0.38	0.64	0.983	0.20	0.37	0.835	0.43	0.56	0.982	0.18
	Std, fluor alcs	0.53	0.56	0.959	0.21	0.26	0.584	0.48	0.43	0.959	0.19
	Std, TFA, fluor alcs	0.40	0.58	0.887	0.34	0.28	0.680	0.45	0.52	0.885	0.32
2-Butyl	Std[d]	0.41	0.71	0.999		0.63	0.888	0.44	0.59	0.999	0.06
	Std,[d] TFA	0.32	0.75	0.993	0.20	0.50	0.900	0.41	0.66	0.992	0.14
2-Pentyl	Std[d]	0.40	0.73	0.999		0.66	0.897	0.43	0.60	0.999	0.05
	Std,[d] TFA	0.30	0.77	0.992	0.22	0.54	0.917	0.39	0.69	0.992	0.16
3-Pentyl	Std	0.41	0.69	0.993	0.19	0.58	0.908	0.38	0.58	0.993	0.13
	Std, TFA	0.26	0.72	0.982	0.28	0.54	0.945	0.34	0.69	0.980	0.24
4-Heptyl	Std[e]	0.33	0.75	0.998		0.69	0.933	0.36	0.66	0.998	0.08
	Std,[e] TFA	0.22	0.80	0.991	0.26	0.64	0.962	0.30	0.76	0.991	0.19
Cyclopentyl	Std[f]	0.37	0.70	0.998		0.55	0.939	0.34	0.60	0.997	0.11
	Std,[f] TFA	0.26	0.71	0.993	0.23	0.51	0.965	0.29	0.67	0.991	0.19
Cyclohexyl	Std	0.32	0.78	0.999	0.08	0.69	0.959	0.29	0.68	0.999	0.05
	Std, TFA	0.22	0.80	0.995	0.16	0.64	0.974	0.27	0.75	0.995	0.14
	Std, fluor alcs	0.33	0.74	0.989	0.15	0.56	0.927	0.30	0.66	0.989	0.13
	Std, TFA, fluor alcs	0.23	0.75	0.975	0.24	0.59	0.950	0.29	0.72	0.974	0.23
Benzyl	Std[g-i]	0.75	0.64	0.971	0.42	0.57	0.80	0.62	0.51	0.972	0.34

[a] Std indicates EtOH, 50 and 80% (vol) aqueous EtOH, AcOH, and HCO_2H. TFA indicates trifluoroacetic acid. Fluor alcs indicates 70 and 97% (wt) aqueous trifluoroethanol and 97% (wt) aqueous hexafluoroisopropanol. [b] Probable error[3h] = $0.6745\sqrt{\Sigma d_i^2/(n-f)}$ where d_i is the absolute value of the difference between the ith calculated and experimental value, n is the number of data being fitted, and f is the number of parameters employed ($f = 4, 2,$ and 3 for eq 3, 1, and 6, respectively). [c] 50 °C. [d] Available EtOH data not employed; see ref 11. [e] EtOH data not available. [f] Data in 50% (vol) aqueous EtOH not available. [g] Reference 3b. [h] H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Am. Chem. Soc.*, **89**, 370 (1967). [i] J. Delhoste, *Bull. Soc. Chim. Fr.*, 133 (1974).

it is a suitable model for limiting k_c solvolyses.[11] Rate constants for 2-adamantyl tosylate plot linearly (correlation coefficient 0.999) with those for p-methoxyneophyl tosylate where common data are available (aqueous $EtOH-HCO_2H$)[3i] and also with those for neophyl tosylate in many solvents including ethanol and trifluoroacetic acid (correlation coefficient 0.993).[3i,22] Fortunately, there is virtually no change in the difference between acetic and formic acid Y values in the *tert*-butyl chloride and 2-adamantyl tosylate scales (3.69 vs. 3.65 Y units), thereby allowing calculation of N values for both Y scales with the same m_{AF} value of 0.3 for methyl tosylate.

To increase the amount of data available to us, additional rate constants for methyl tosylate in aqueous acetone and dioxane solvents were estimated from results for ethyl benzenesulfonate and an empirical correlation (eq 9)

$$\log k_{CH_3OTs} = 0.81 \log k_{EtOSO_2Ph} - 0.80 \qquad (9)$$

of methyl tosylate vs. ethyl benzenesulfonate in alcoholic and mixed aqueous solvents: MeOH, EtOH, i-PrOH, 50 and 80% (vol) aqueous EtOH, H_2O, 56% (wt) aqueous acetone, and 50, 80, and 90% (wt) aqueous dioxane (correlation coefficient 0.995).[23] Table I summarizes values of N and Y in a wide range of solvents for both the 2-adamantyl tosylate and *tert*-butyl chloride scales, and except for trifluoroacetic acid the two sets of N constants are very similar. Addition of water or ethanol to trifluoroethanol markedly increases the nucleophilicity of the medium.

Correlations Using Equation 3 and Equation 6. Table III summarizes the correlations by eq 3 and eq 6 of solvolysis rates for primary and secondary substrates in solvents varying in nucleophilicity and ionizing power from ethanol to trifluoroacetic acid.[24] Correlation coefficients are greater than 0.97 in all but two cases. The average value of the probable error,

r,[25] of log k/k_0 for all compounds in the standard group of solvents and trifluoroacetic acid is 0.21 (eq 3) and 0.17 (eq 6), indicating that solvolysis rate constants can usually be calculated well within a factor of 3. This agreement is very good considering the wide range of solvents, different sources of data, and extrapolation of rate data to common temperatures. Equation 1, which contains a term for solvent ionizing power but not for solvent nucleophilicity, gives much poorer correlations; even for all secondary compounds in the same set of solvents (std, TFA), the average value of the probable error, r, is 0.32 and worsens when the data for a primary substrate, ethyl, are included (0.39). Figures 1–3 provide a comparison of the three treatments (eq 1, 3, and 6) but, because rate constants calculated from eq 3 and eq 6 are very similar, only results from eq 1 and eq 3 are plotted.

Since both eq 3 and 6 contain terms for methyl tosylate and 2-adamantyl tosylate, the adjustable parameters l, m, and Q are interrelated. Using eq 3, 6, and 8, and footnote d of Table I, it can be shown that:

$$l = 1 - Q \qquad (10)$$

$$m = 0.3 + 0.7Q \qquad (11)$$

$$l = (1 - m)/0.7 \qquad (12)$$

These simple relationships between eq 3 and 6 assume that the experimental data fit the equations perfectly. Although this situation is clearly not true in practice, plots of m vs. Q and l vs. $(1 - m)$ are in good agreement with the ideal solutions—eq 11 and 12.

The interrelation of these values provides additional evidence for the merging of mechanism and reactivity deduced from Figure 3 of the preceding paper.[11] Also the values of m from eq 3 (Table III) are in good agreement with m_{AF} values (Table
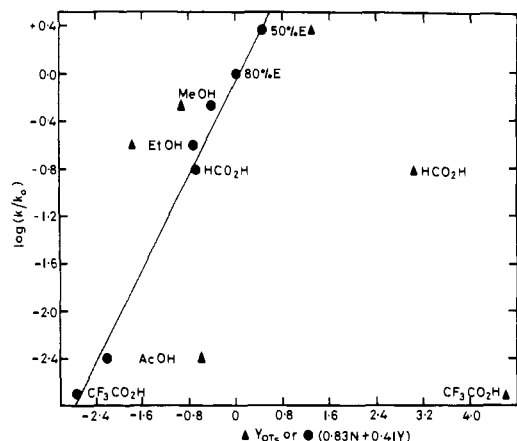
Figure 1. Correlation of log (k/k_0) for ethyl tosylate against $Y_{2\text{-AdOTs}}$ alone vs. $(0.83N_{OTs} + 0.41Y_{2\text{-AdOTs}})$.

Figure 2. Correlation of log (k/k_0) for 2-propyl tosylate against $Y_{2\text{-AdOTs}}$ alone vs. $(0.4N_{OTs} + 0.58Y_{2\text{-AdOTs}})$.

V, ref 11), showing that the different mechanistic criteria agree quantitatively.

Implications for Solvolysis Mechanisms. Magnitude of Nucleophilic Solvent Assistance. Table III shows that the fit of data for primary *and* secondary substrates is improved considerably when a term for solvent nucleophilicity is introduced (eq 3 and 6). These results strongly imply that solvent is a kinetically significant nucleophile in the overall solvolytic processes of simple primary and secondary substrates.[11] Table III also shows that l (eq 3) decreases and Q (eq 6) increases as the incipient positive charge becomes more stable and more hindered to nucleophilic attack. However, even for cyclohexyl, l (0.22) is of significant magnitude, and m (0.80) and Q (0.75) are less than for 2-adamantyl ($m = Q = 1.0$, defined), our model for k_c solvolysis. Thus, solvolyses of cyclohexyl substrates are susceptible to nucleophilic attack.

Minimum estimates of the *magnitude* of nucleophilic solvent assistance, k_s/k_c, for solvolysis of any tosylate (ROTs) can be calculated from eq 13

$$k_s/k_c = [k_t(ROTs)/k_t(2\text{-AdOTs})]_{\text{any solvent}}/$$
$$[k_t(ROTs)/k_t(2\text{-AdOTs})]_{CF_3CO_2H} \quad (13)$$

(Table IV), which is based on the following evidence and assumptions:[21,26] (i) solvolysis of 2-adamantyl tosylate in any solvent is a k_c process,[6] i.e., is not accelerated by nucleophilic solvent assistance;[7] (ii) solvolysis of any secondary tosylate in CF_3CO_2H is a k_c process;[21] (iii) the rate constant for solvolysis of any tosylate (ROTs) relative to 2-adamantyl tosylate in any solvent, $[k_t(ROTs)/k_t(2\text{-AdOTs})]_{\text{any solvent}}$, increases from the limiting k_c value of $[k_t(ROTs)/k_t(2\text{-AdOTs})]_{CF_3CO_2H}$ solely because of the nucleophilic solvent assistance.

The likely direction of small errors in the above assumptions is such that the estimates of k_s/k_c are minimum values (vide infra). *Solvolyses with $k_s/k_c > 10$ (Table IV) appear to be nucleophilically solvent assisted because the 23 500-fold variation in k_s/k_c can be quantitatively accounted for, within a small rate factor (<10) using eq 3*, which explicitly accounts for the effects of solvent nucleophilicity and ionizing power.

Because of uncertainties in our correlations (eq 3 and eq 6), it is necessary to consider the possibility that a small amount of internal return from ion pair intermediates (reducing k_t by a factor of 5 or less) may occur [e.g., in trifluoroethanolyses of 2-propyl tosylate (Figure 2) and cyclohexyl tosylate (Figure 3)].[27,28] Although there are other explanations (vide infra), this may account for the small but apparently systematic deviations from our correlations in fluorinated alcohols and may be similar to deviation observed in *tert*-butyl chloride solvolyses.[9b,9e] However, there is no satisfactory evidence that hidden return occurs in any 2-adamantyl solvolyses[29] or in trifluo-
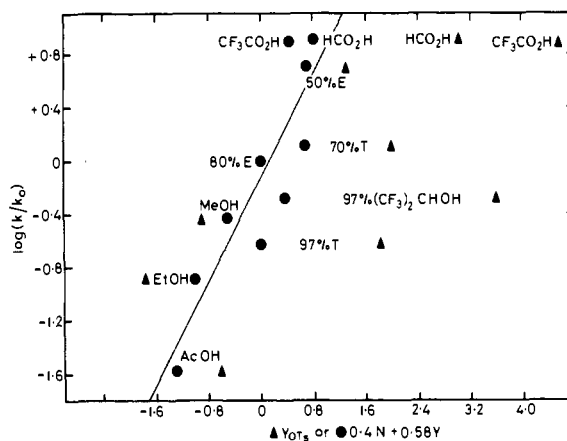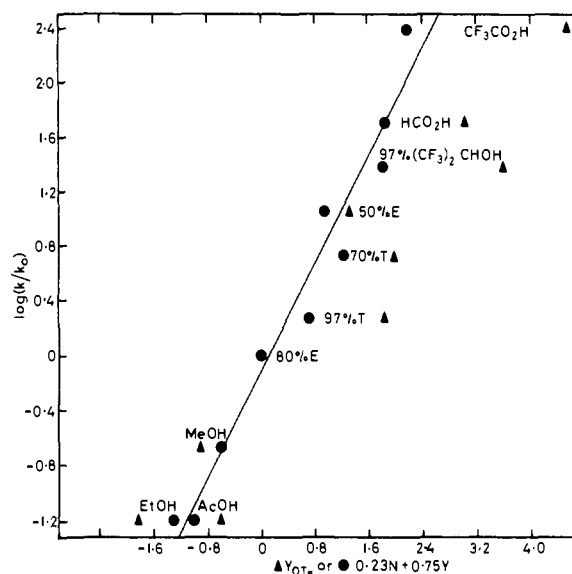

Figure 3. Correlation of log (k/k_0) for cyclohexyl tosylate against Y_{OTs} alone vs. $(0.23N_{OTs} + 0.75Y_{2\text{-AdOTs}})$.

roacetolysis of 2-propyl tosylate.[30-32] Thus, if titrimetric rate constants for trifluoroethanolysis of 2-propyl tosylate were reduced by a factor of 5 by hidden return, the magnitude of nucleophilic solvent assistance (k_s/k_c) would be five times greater than calculated, i.e., $5 \times 15.3 = 76.5$. In general, k_s/k_c values (Table IV) would have to be multiplied by the rate factors due to hidden return (≥ 1) to give a more accurate estimate of the magnitude of nucleophilic solvent assistance.[33] We wish to stress that evidence presented in this and the preceding paper[11] argues against hidden return of substantial magnitude (>5).

However, as nucleophilic solvent assistance might be expected to help to prevent hidden return,[11] deviations from our correlations may be better explained by electrophilic solvation of the leaving group. Our implicit assumption that one parameter (m or Q) accounts for each substrate's sensitivity to both general solvent power and electrophilic solvation ion of the leaving group may not be completely justified. In trifluoroacetic acid the effect of electrophilic solvation may be unusually high, which could explain why the values of l, m, and Q change slightly when trifluoroacetic acid is included in the correlations (Table III). Although the importance of electrophilic solvation of the leaving group is well established,[3] we do not believe that it would be appropriate at the present time to introduce another adjustable parameter to account explicitly for it.

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Table IV. Minimum Estimates of Nucleophilic Solvent Assistance $(k_s/k_c)^a$

Tosylates	CF$_3$CO$_2$H	97 wt % (CF$_3$)$_2$CHOH	97 wt % CF$_3$CH$_2$OH	HCO$_2$H	70 wt % CF$_3$CH$_2$OH	AcOH	50% EtOH	80% EtOH	EtOH
2-Adamantyl[b]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0[c]
Pinacolyl[d,e]	1.0		3.6	2.4[f]	3.2	8.6	9.5[f]	12	
Cyclohexyl	1.0	0.62	3.2	5.0	6.6	28	61	104	256
Cyclopentyl	1.0			10		105		455	1680
4-Heptyl	1.0	0.87[g]		3.9		28	46	146	
3-Pentyl	1.0	0.60[g]		6.2		46	103	310	1310
2-Pentyl	1.0			9.6		88	195	616	
2-Butyl[e]	1.0		6.3	13	22	140	292	979	
2-Propyl[e]	1.0	0.57	15.3	32	57	472	1130	4430	23 500

^{a} Rate factors calculated from eq 13 using data in Table II and reference 11 (Table III). ^{b} Solvolysis not sensitive to solvent nucleophilicity. ^{c} Using $m = 0.78$ (eq 1) at 25° $k = 6 \times 10^{-10}$ s^{-1}—extrapolated experimental value $k = 4.3 \times 10^{-10}$ s^{-1} reference 11—Table II. ^{d} Calculated from rate constants for the brosylate assuming OBs/OTs rate ratio = 5.0 in ethanol/water and 3.0 in other solvents—reference 11, see also reference 28. ^{e} See also A. Pross and R. Koren, *Tetrahedron Lett.*, 1949 (1974), this work largely agrees with our results but uses less reliable experimental data for solvolysis of 2-adamantyl tosylate in formic acid—see reference 11 (Table II). ^{f} Reference 28 uses less reliable experimental data for 2-adamantyl solvolyses. ^{g} Reference 21b.

Structures of Ion Pair Intermediates. The precision of the correlations using only one or two adjustable parameters (eq 6 and 3, respectively) is sufficiently good that these results strongly suggest the importance of nucleophilic solvent assistance. It has been suggested that an intimate ion pair intermediate is formed prior to nucleophilic attack by solvent.[18] Shiner and co-workers proposed this mechanism for solvolyses of simple secondary substrates in weakly nucleophilic solvents (e.g., acetic, formic, and trifluoroacetic acids and trifluoroethanol).[27] Such ion pair intermediates are represented as having an extended bond with considerable ionic character, *without nucleophilic solvation at the rear.* On the basis of the magnitude of α-D isotope effects, Shiner suggests that as many as four different steps in secondary solvolyses can be rate determining;[27] for 2-propyl brosylate: direct nucleophilic attack (S$_N$2) (k_4, 80% (vol) aqueous EtOH to EtOH), formation of the ion pair (k_1, water to 70% (vol) aqueous EtOH), nucleophilic attack on the ion pair (k_5, 97% (wt) trifluoroethanol), and dissociation of the ion pair (k_2, trifluoroacetic acid), Scheme I.

Scheme I
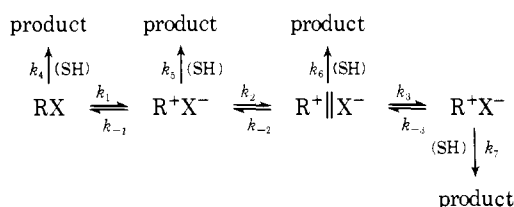
Rather than this "quantized" approach to solvolysis with several different rate-limiting steps, we favor the interpretation that there exists a continuum of nucleophilic solvation between the methyl and 2-adamantyl extremes,[1,11] which lead to various substitution or elimination products. We have already presented a variety of independent arguments to show that Shiner's interpretation is not consistent with our experimental evidence.[11,31] In addition, α-D isotope effects for 2-propyl brosylate in solvents from 90% (vol) aqueous ethanol to trifluoroacetic acid give fair correlations directly with solvent nucleophilicity constants, N, or values of log (k_s/k_c), correlation coefficients 0.969 and 0.952, respectively (see also Figure 4). Thus, our interpretation (Scheme I, preceding paper), adequately explains Shiner's experimental evidence, without postulating four different rate-limiting steps. We, therefore, feel that the *specific exclusion of nucleophilic solvent assis-*

tance *during formation of secondary ion pairs provides an energetically less feasible alternative and is not correct.*[34]

Structural Effects on Absolute Rates. The above interpretation of the solvent effect on relative rates necessitates reconsideration of much earlier work in the literature which assumed that the acetolysis of secondary tosylates proceeded by S$_N$1 or limiting (i.e., carbenium ion or nonnucleophilically solvated ion pair) mechanisms.[35] The minimum estimates of nucleophilic solvent assistance (Table IV) show that rate ratios of at least 470 may be due to nucleophilic solvent assistance in acetolysis of 2-propyl tosylate. More hindered cyclic structures (e.g., cyclohexyl) are less strongly, but still substantially, nucleophilically assisted.

2-Butyl tosylate reacts slightly more rapidly than 2-pentyl and 3-pentyl more rapidly than 4-heptyl in all solvents except trifluoroacetic acid (preceding paper, Table III). The order of solvolysis rates expected from the gas-phase stabilities of carbenium ions,[36] i.e., 4-heptyl > 3-pentyl > 2-pentyl > 2-butyl > 2-propyl, is only achieved in trifluoroacetic acid and hexafluoroisopropanol,[21] indicating the importance of solvent nucleophilicity in determining relative rates.

Comparison of the rates of solvolysis of 2-propyl and 2-butyl tosylates in trifluoroacetic acid shows that the electron-donating effect of a β-methyl group in the 2-propyl cation ion pair is a factor of about 6 (14.6/2.49).[37] Presumably, this is greater than the factor of 2–3 for acetolysis and formolysis because of the greater intramolecular electronic demands of the very weakly nucleophilically solvated transition state for trifluoroacetolysis. These inductive/hyperconjugative effects can be correlated using the Taft σ^* treatment, which was the basis of one of our arguments against appreciable "hidden return" in the secondary solvolyses.[31] According to this interpretation, *solvolyses of secondary tosylates in trifluoroacetic acid are very weakly nucleophilically solvent assisted (if at all) and show enhanced inductive/hyperconjugative effects, and the rates are not complicated by appreciable hidden return.*

To compare relative solvolysis rates in other solvents, it is necessary to correct for nucleophilic solvent assistance. In principle this may be done using k_s/k_c ratios, but there is a potential danger. If only one solvent (e.g., acetic acid) is selected, the conclusions are subject to experimental error, particularly if experimental data from different laboratories and/or extrapolation from different temperatures are used. It would be more reliable to compare k_s/k_c in several solvents or estimate the "overall" role of nucleophilic solvent assistance using the "Q" equation (6). Values of Q (eq 6), measuring the *sensitivity* to solvent nucleophilicity relative to methyl and

2-adamantyl, for the secondary substrates in Table III plot linearly with log (k_s/k_c ratios), correlation coefficient >0.975 for each solvent.
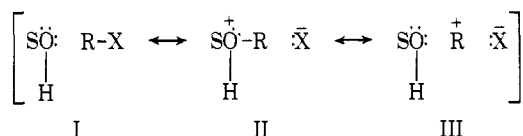
Limitations of Equations 1, 3, and 6. Because scales of ionizing power do not explicitly account for electrophilic solvation of the leaving group,[3h] we have only studied tosylates in this work. Research in progress will extend these correlations to other leaving groups. The inadequacies of eq 1 for SN2 solvolyses are apparent from the above discussion and earlier work.[3]

Equation 6 can be used to correlate a spectrum of reactivities between any two substrates chosen as standards. If methyl bromide and *tert*-butyl chloride are used as standards A and B, respectively, eq 6 can be rearranged to eq 14, which re-

$$\log (k/k_0) - \log (k/k_0)_A = Q[\log (k/k_0)_B - \log (k/k_0)_A]$$
$$(14)$$

sembles eq 5 of Swain and co-workers.[14] Both Q (eq 6) and a (eq 5) are substrate parameters measuring the sensitivity to solvent nucleophilicity, and $b = \log (k/k_0)_B - \log (k/k_0)_A$ when eq 5 is evaluated for *tert*-butyl chloride ($a = 1$). A basic difference in the two approaches is that we have chosen to adjust only Q, while Swain and Dittmer iteratively varied both a and b in order to obtain the best fit for all substrate–solvent data treated. Because in its present form eq 6 assumes an SN2–SN1 ($k_s - k_c$) spectrum of reactivities, it should not be used to correlate k_Δ solvolyses.

The limitations of eq 3 an other limitations of eq 6 are more subtle and difficult to define. The possibility that electrophilic solvation effects are not adequately accounted for has already been discussed. Also the condition for transformation of eq 2 to eq 3, that the terms $(\partial \log k/\partial N)_Y$ and $(\partial \log k/\partial Y)_N$ be constant and equal to l and m, respectively, is not completely valid. Winstein suggested that the rate-determining step of solvolysis could be described as a hybrid of three resonance structures, I–III.[3b,20] Variation of solvent nucleophilicity or

$$\left[\begin{array}{ccc} \overset{..}{SO:} R-X & \longleftrightarrow & \overset{..}{SO}-R \quad :\bar{X} & \longleftrightarrow & \overset{..}{SO:} \quad \overset{+}{R} \quad :\bar{X} \\ | & & | & & | \\ H & & H & & H \end{array} \right]$$

$$\quad\quad I \quad\quad\quad\quad\quad\quad II \quad\quad\quad\quad\quad\quad III$$

solvent ionizing power even at constant Y or N, respectively, can alter the relative contributions of structures I–III and the values of the differential terms. For example, where solvents have the same nucleophilicity but different ionizing powers, such as acetic and formic acids ($\Delta Y = 3.7$), solvolysis in the medium of higher ionizing power (formic acid) might occur through a transition state with a smaller relative contribution of structure II. In support of this interpretation k_s/k_c ratios (Table IV) in formic acid are less than in acetic acid and values of m_{AF} for simple alkyl substrates are usually larger than values of $m_{aq\ EtOH}$.[38,39]

Thus, m and l are not constant for a substrate subject to varying amounts of nucleophilic solvent assistance, and their variations appear to be interrelated (eq 10, 12, structures I–III). Although l and m reported here using eq 3 must necessarily be "average" values which give the best fit for the data, they are indicative of the overall sensitivity of particular substrates to solvent nucleophilicity and ionizing power and do provide improved correlations over eq 1. Methyl solvolyses in which structure II makes a large contribution should be least prone to such changes ($m_{aq\ EtOH} = 0.23$, $m_{AF} = 0.3$) and should provide a suitable scale of solvent nucleophilicity just as tertiary solvolyses, dominated by structure III, do for solvent ionizing power.

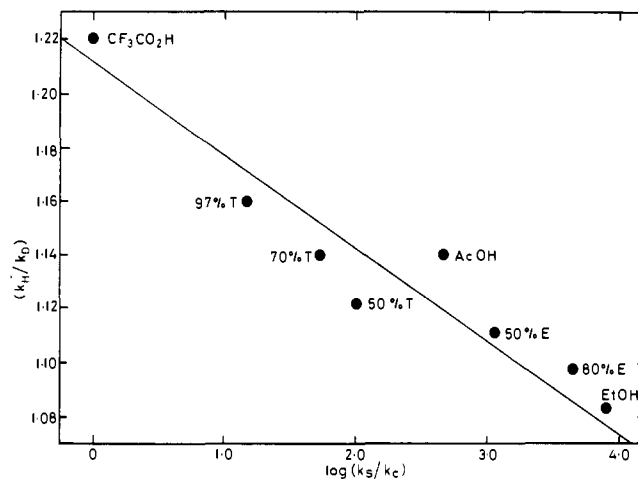A frequent problem in structure/reactivity correlations is

Figure 4. Correlation of α-deuterium isotope effects (k_H/k_D) for 2-propyl brosylate against the magnitude of solvent assistance [log (k_s/k_c)] in various solvents.

the complex relationship among activation parameters.[3d] There is no consistent pattern discernible for the activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) for the solvolyses discussed in this paper, as would be expected when the structural variation (i.e., solvent) studied in the series is at the reaction site.[40] Therefore, these correlations cannot be expected to fit precisely, because relative rates are temperature dependent when reactions with different $\Delta H^\ddagger$ are compared, e.g., a difference ($\Delta \Delta H^\ddagger$) of 3 kcal/mol causes a change in relative rate of a factor of 3 when the temperature changes from 25 to 100 °C.[13,41]

Considering these limitations and the complexity of solvation effects, the precision of the correlations is very good and small deviations cannot be interpreted simply and reliably.

Conclusions

The ability to calculate accurately solvolysis rate constants in a wide solvent range has been a goal of physical organic chemistry for the past 25 years.[3a] During this period, considerable refinements have been made to mechanistic details of the solvolytic process in the SN2–SN1 spectrum of Hughes and Ingold,[18] and it is now clear that the role of solvent as kinetically significant nucleophile has previously been underestimated.

Solvolyses with k_s/k_c (Table IV) greater than a factor of about 10 are significantly nucleophilically solvent assisted and should be classified as SN2, consistent with this interpretation, all carefully studied cases are known to involve substitution with essentially complete inversion of configuration. Further work is required to confirm details of the above conclusions, but it is also clear that acetolyses of most secondary tosylates should be classified as SN2 or SN2(intermediate) reactions, $k_s/k_c > 10$ (Table IV). For example, in acetic acid, 2-propyl is assisted by a factor of 470 and cyclohexyl by a factor of 28. A reassessment of much previous work on the structure–reactivity correlations is required.

Solvolyses of all secondary tosylates in trifluoroacetic acid and hexafluoroisopropanol appear to involve little or no nucleophilic solvent assistance ($k_s/k_c \sim 1$). The increased carbenium ion character of these SN1 reactions causes enhanced inductive/hyperconjugative substituent effects of adjacent atoms.

All the kinetic data can be quantitatively correlated within a small rate factor by solvent nucleophilicity and ionizing power terms. Additional postulates such as (hidden) internal return from intimate ion pairs[27] are not required. This supports other evidence[11] that these effects may not contribute greatly to the overall kinetic results.

Experimental Section

General. All boiling points are uncorrected. Melting points (also uncorrected) were determined using a Mettler FPI Apparatus. Microanalyses were performed by Hoffmann-La Roche, Inc., Nutley, N.J.

Materials. Tosylates. Methyl tosylate (Eastman) was recrystallized five times. Other tosylates, prepared from high purity alcohols and p-toluenesulfonyl chloride in the usual manner,[42] were recrystallized several times from petroleum ether/chloroform at −78 °C, and their purity was confirmed by elemental analysis: 2-adamantyl tosylate, mp 82.1–83.4 °C (lit.[43] mp 82.7–83.7 °C); cyclohexyl tosylate, mp 44.1–45.4 °C (lit.[44] 43.5–44.0 °C).

Solvents. Dioxane was purified by the method of Fieser.[45] The purified solvent was stored over sodium and distilled shortly before use. Trifluoroethanol (B and A) was purified in the manner of Shiner et al.[9a] Hexafluoroisopropanol (B and A or du Pont) was stored for 2 days over Fisher 3A molecular sieves, decanted onto fresh molecular sieves,[46] and distilled, bp 59.1 °C.

Kinetic Methods. Rates in aqueous trifluoroethanol and hexafluoroisopropanol were determined conductimetrically with a Wayne-Kerr Model B331 impedence bridge or a recording Wheatstone bridge,[47] as described previously.[11]

Kinetics in aqueous dioxane were performed by the usual sealed ampule technique[48] (initial substrate concentration, 0.03 M), titrating the liberated p-toluenesulfonic acid with standard NaOH and phenolphthalein. Unless oxygen is rigorously excluded, the infinity titer increases with time, apparently as the result of acid-catalyzed oxidation of the dioxane.[49] Thus, nitrogen was bubbled into the solution in each ampule (normally 9 per run) through a thin-glass tube for several seconds, and the ampule was sealed immediately.[50] Experimental infinity titers were 1–2% greater than the calculated values.

Raw kinetics data were fitted to the first-order rate equation by means of a modified version of the LSKIN least-squares computer program.[51]

References and Notes

(1) A preliminary account of this work has been published: T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, J. Am. Chem. Soc., **94**, 992 (1972).

(2) (a) National Science Foundation Trainee 1968–1969; National Institutes of Health Predoctoral Fellow 1969–1974; (b) NATO Postdoctoral Research Fellow, 1969–1971.

(3) (a) E. Grunwald and S. Winstein, J. Am. Chem. Soc., **70**, 846 (1948); for further solvent effect studies in this series, see: (b) S. Winstein, E. Grunwald, and H. W. Jones, ibid., **73**, 2700 (1951); (c) A. H. Fainberg and S. Winstein, ibid., **78**, 2770 (1956); (d) S. Winstein and A. H. Fainberg, ibid., **79**, 5937 (1957); (e) A. H. Fainberg and S. Winstein, ibid., **79**, 1597 (1957); (f) A. H. Fainberg and S. Winstein, ibid., **79**, 1602 (1957); (g) A. H. Fainberg and S. Winstein, ibid., **79**, 1608 (1957); (h) S. Winstein, A. H. Fainberg, and E. Grunwald, ibid., **79**, 4146 (1957); (i) S. G. Smith, A. H. Fainberg, and S. Winstein, ibid., **83**, 618 (1961).

(4) In this equation and other equations in this paper, k and k_0 are rate constants for the substrate in any solvent and in 80% (vol) aqueous ethanol, respectively, and m measures the sensitivity of the substrate to solvent ionizing power, Y.

(5) Generally, solvolyses lead to both substitution and elimination (as well as to rearrangement) products in relative yields which vary markedly with substrate, solvent, and temperature. Hence, our discussion is relevant to SN2, SN1, E2, and E1 mechanisms.

(6) Although the term k_c is often applied to solvolyses proceeding without detectable nucleophilic solvent assistance to formation of the first transition state,[7,8] strictly speaking it should designate the (hypothetical) limit where nucleophilic solvent assistance is exactly zero ("limiting solvolyses"). As the magnitude of nucleophilic solvent assistance may decrease exponentially without actually becoming zero, it would be difficult if not impossible to determine experimentally whether the "limit" is actually reached. Thus solvolyses of substrates such as 2-adamantyl tosylate or tert-butyl chloride, where nucleophilic solvent assistance cannot be detected, are models for k_c behavior, but it is difficult to determine whether nucleophilic solvent assistance is exactly zero. Nucleophilically solvent-assisted processes are designated k_s and anchimerically assisted processes are designated k_Δ. See S. Winstein, E. Allred, R. Heck, and R. Glick, Tetrahedron, **3**, 1 (1958).

(7) We define nucleophilic solvent assistance as that bonding of solvent as nucleophile or base (as distince from general electrostatic solvation) to any atom of the substrate (e.g., α-carbon, β-hydrogen, etc.) which contributes significantly to the kinetics of solvolysis.

(8) There is no general agreement on nomenclature for more complex mechanisms, e.g., when the rate of internal return is comparable with the rate of nucleophilic attack on or elimination from the first formed k_c ion pair, which may occur in trifluoroethanolyses of tert-butyl chloride.[9,10]

(9) (a) V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, J. Am. Chem. Soc., **91**, 4838 (1969); (b) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, ibid., **92**, 5977 (1970); (c) D. E. Sunko, I. Szele, and M. Tomic, Tetrahedron Lett., 1827 (1972); (d) D. E. Sunko and I. Szele, ibid., 3617 (1972); (e) J. M. Harris D. J. Raber, W. C. Neal, Jr., and M. D. Dukes, ibid., 2331 (1974).

(10) (a) Z. Rappoport and J. Kaspi, J. Am. Chem. Soc., **96**, 586 (1974); (b) Z. Rappoport and J. Kaspi, ibid., **96**, 4518 (1974); (c) P. Haake and P. S. Ossip, ibid., **93**, 6924 (1971).

(11) T. W. Bentley and P. v. R. Schleyer, J. Am. Chem. Soc., preceding paper in this issue, and references there cited.

(12) C. G. Swain, R. B. Mosely, and D. E. Bown, J. Am. Chem. Soc., **77**, 3731 (1955).

(13) A. J. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962.

(14) (a) C. G. Swain and D. C. Dittmer, J. Am. Chem. Soc., **75**, 4627 (1953); (b) C. G. Swain, D. C. Dittmer, and L. E. Kaiser, ibid., **77**, 3737 (1955).

(15) For reviews, see (a) J. F. Bunnett, Annu. Rev. Phys. Chem., **14**, 271 (1963); (b) K. M. Ibne-Rasa, J. Chem. Educ., **44**, 89 (1967); (c) S. R. Hartshorn, "Aliphatic Nucleophilic Substitution", Cambridge University Press, 1974, pp 48–52; (d) C. D. Ritchie, Acc. Chem. Res., **5**, 348 (1972).

(16) For general discussions of empirical measures of solvent polarity, see (a) E. M. Kosower, "An Introduction to Physical Organic Chemistry", Wiley, New York, N.Y., 1968, pp 293–333; (b) C. Reichardt, Angew. Chem., Int. Ed. Engl., **4**, 29 (1965).

(17) (a) F. L. Schadt and P. v. R. Schleyer, J. Am. Chem. Soc., **95**, 7860 (1973); (b) F. L. Schadt and P. v. R. Schleyer, to be submitted for publication; (c) F. L. Schadt, C. J. Lancelot, and P. v. R. Schleyer, to be submitted for publication; (d) D. J. Raber, M. D. Dukes, and J. Gregory, Tetrahedron Lett., 667 (1974).

(18) The mechanistic background to this work is discussed in the preceding paper.[11]

(19) P. E. Peterson and F. J. Waller, J. Am. Chem. Soc., **94**, 991 (1972).

(20) S. Winstein and H. Marshall, J. Am. Chem. Soc., **74**, 1120 (1952).

(21) (a) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, Tetrahedron Lett., 2335 (1974); (b) L. Shoer, unpublished results in 97% hexafluoroisopropanol.

(22) A. Diaz, I. Lazdins, and S. Winstein, J. Am. Chem. Soc., **90**, 6546 (1968).

(23) For data see Table II and Table I, footnotes g, k, l, and n.

(24) Kinetic data is tabulated in Table II of this paper and Table III of ref 11.

(25) See Table III, footnote b.

(26) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, J. Am. Chem. Soc., **92**, 2542 (1970).

(27) (a) V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, J. Am. Chem. Soc., **91**, 7748 (1969); (b) V. J. Shiner, Jr., and R. D. Fisher, ibid., **93**, 2553 (1971); (c) V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions", C. J. Collins and N. S. Bowman, Ed., Van Nostrand–Reinhold, New York, N.Y., 1970.

(28) J. E. Nordlander, R. E. Gruetzmacher, and F. Miller, Tetrahedron Lett., 927 (1973).

(29) See discussion of Table IV and Figure 2 in preceding paper (ref 11).

(30) See σ* plot, Figure 1 (ref 31) and Table III.

(31) T. W. Bentley, S. H. Liggero, M. A. Imhoff, and P. v. R. Schleyer, J. Am. Chem. Soc., **96**, 1970 (1974).

(32) Combining the recently revised rate constant for trifluoroacetolysis of pinacolyl tosylate (4.09×10^{-3} s^{-1}, ref 28) with Shiner's previous argument[27] gives a revised maximum rate factor of 16 due to hidden return for trifluoroacetolysis of 2-propyl tosylate. However, this argument does not allow for enhanced inductive effects in weakly nucleophilic media.[31]

(33) As the k_s/k_c values for 2-propyl, 3-pentyl, and 4-heptyl tosylates in CF_3CO_2H and 97% $(CF_3)_2CHOH$ are equal to or close to unity (Table IV), we conclude that these solvolyses are essentially limiting.[21]

(34) M. H. Abraham, J. Chem. Soc., Perkin Trans. 2, 1893 (1973); see also F. G. Bordwell et al., J. Am. Chem. Soc., **97**, 118, 123, 127, 132 (1975).

(35) C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer in "Carbonium Ions", Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1972, p 1475, and references there cited.

(36) F. P. Lossing and G. P. Semeluk, Can. J. Chem., **48**, 955 (1970); L. Radom, J. A. Pople, and P. v. R. Schleyer, J. Am. Chem. Soc., **94**, 5935 (1972).

(37) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, J. Am. Chem. Soc., **87**, 5169 (1965).

(38) Table V, preceding paper (ref 11).

(39) However, the higher m_{AF} values may also be due to greater electrophilic solvation of the leaving group in formic acid than in acetic acid.

(40) L. P. Hammett in "Physical Organic Chemistry", McGraw-Hill, New York, N.Y., 1970, Chapter 12.

(41) $\Delta \Delta H^{\ddagger}$ for 2-adamantyl solvolyses varies over at least 12 kcal/mol with change in solvent; see Table II of this and the preceding paper.

(42) L. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967, p 1179.

(43) P. v. R. Schleyer and R. D. Nicholas, J. Am. Chem. Soc., **83**, 182 (1961).

(44) S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, J. Am. Chem. Soc., **70**, 816 (1948).

(45) L. F. Fieser, "Experiments in Organic Chemistry", D. C. Heath, Boston, Mass, 1941.

(46) M. A. Matesich, J. Knoefel, H. Feldman, and D. F. Evans, J. Phys. Chem., **77**, 366 (1973).

(47) C. J. Lancelot, Ph.D. Thesis, Princeton University, 1971.

(48) S. Winstein, C. Hanson, and E. Grunwald, J. Am. Chem. Soc., **70**, 812 (1948).

(49) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, J. Am. Chem. Soc., **93**, 4821 (1971).

(50) E. Tommila and E. Merikallio, Suom. Kemistil. B, **26**, 79 (1953).

(51) D. F. Detar in "Computer Programs for Chemistry", Vol. I, D. F. Detar, Ed., W. A. Benjamin, Inc., New York, N.Y., 1968, pp 126–173; W. F. Sliwinski, Ph.D. Thesis, Princeton University.
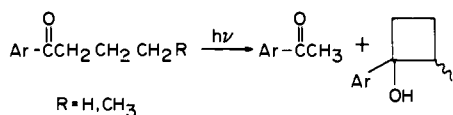
Effects of Methyl Substitution on the Photoreactivity of Phenyl Ketones. The Inapplicability of Hammett σ Values in Correlations of Excitation Energies

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Abstract: The photoreactivity of various ring-methylated butyrophenones and valerophenones is correlated with the effects of methyl substitution on the triplet energy of benzoic acid. *meta*-Methyl substitution stabilizes the π,π^* triplets of the benzoyl chromophore somewhat more than does para substitution. *para*-Methyl substitution destabilizes n,π triplets whereas *meta*-methyls have at most a slight effect. As the energy difference ΔE_T between n,π^* and π,π^* triplets of the methylated ketones increases, the observed rate constant for triplet-state hydrogen atom abstraction decreases and is proportional to $\exp(-\Delta E_T/RT)$. No evidence for vibronic mixing induced reactivity in π,π^* ketone triplets is apparent; all reactivity seems to arise from equilibrium levels of the upper n,π^* states. The results illustrate the inapplicability of Hammett σ values in correlations of excited-state reactivity.

It is now well established that ketones with π,π^* lowest triplets are appreciably less reactive than those with n,π^* triplets in hydrogen-abstraction reactions, both intermolecular[1-3] and intramolecular.[4,5] In cases where the two triplets are close enough in energy to equilibrate thermally before decaying, hydrogen abstraction can occur from low concentrations of n,π^* triplets even when the π,π^* triplets are lower.[5,6] It has also been suggested[3] that vibronic mixing[7,8] of the two triplets might induce n,π^*-like reactivity in the lowest triplet. Despite the lack of any theoretical or experimental evidence on the quantitative extent of state mixing induced by vibronic coupling, it is certain that coupling is maximal when the energy gap separating the two triplets is minimal. Methyl groups are the most weakly electron-donating substituents in terms of their effects on the π,π^* excitation energies of benzene.[5,9] Consequently we have systematically varied the number and positions of methyl groups on butyrophenone and valerophenone. Normal analysis of triplet lifetimes and type II quantum yields[5,10] has allowed us to measure reactivity as a function of $^3n,\pi^* - {}^3\pi,\pi^*$ energy gaps.

$$\text{Ar-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_2\text{R} \xrightarrow{h\nu} \text{Ar-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{CH}_3 + \underset{\underset{\displaystyle \text{Ar}}{}}{\square}\text{OH}$$

$$\text{R = H,CH}_3$$

Results

Quantum Yield and Quenching Measurements. Degassed benzene solutions 0.1 M in one of the ketones listed in Table I were irradiated at 313 nm to conversions of 5–10%. Quantum yields of substituted acetophenone and cyclobutanol formation were determined relative to a valerophenone actinometer.[10] Quantum yields were lower when low concentrations of 2,5-dimethyl-2,4-hexadiene were present. Stern–Volmer plots of ϕ^0/ϕ vs. diene concentration were linear; their slopes yield $k_q\tau$ values. With k_q equal to 5×10^9 M^{-1} s^{-1},[11] triplet decay rates $(1/\tau)$ listed in the table were calculated. Quantum yields were also determined as a function of added pyridine concentration;[12] the maximum values (observed at 0.5–1.0 M pyridine) are listed in the table. Low concentrations (<0.5 M) of added alcohols also increased quantum yields, but higher concentrations often decreased them, as observed earlier.[5] In most of the ketones, acetophenone and cyclobutanol products accounted for all of the reacted ketone. Only in the case of 3,5-dimethylbutyrophenone was the quantum yield for ketone disappearance significantly higher (by 13%) than that of type II product formation. No other products could be detected.

The quantum yields of 4-methyl- and 3,5-dimethylbutyrophenone and of 3,4-dimethylvalerophenone decreased slightly with increasing ketone concentration over the range 0.05–0.2 M. The quantum yields for the other ketones were invariant over that concentration range.

Spectroscopic Studies. Uv spectra of each ketone in heptane were measured; λ_{max} energies are listed in Table II. All ketones phosphoresce strongly at 77 K, but our apparatus could not resolve the band structure in the more heavily substituted ketones. Phosphorescence spectra for the various methylated benzoic acids were recorded in ethanol. These all showed vibrational spacings of 1020 and 1540 cm^{-1}. The 0–0 band energies are recorded in Table II. The phosphorescence of ethyl benzoate at 77 K was identical in a rigid MCIP glass and in an isopentane slush.
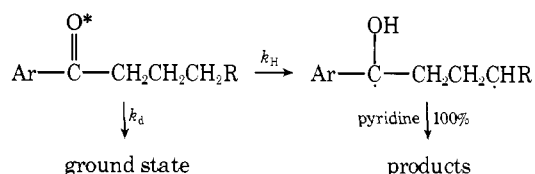
Discussion

Triplet-state rate constants were determined as usual[10] from eq 1. It is assumed that pyridine prevents disproportionation

$$k_H = \Phi_{max}/\tau \qquad (1)$$

$$1/\tau = k_H + k_d \qquad (2)$$

of the diradical[12] intermediate such that any residual quantum inefficiency results from another triplet decay process (rate $= k_d$) competing with γ-hydrogen abstraction (rate $= k_H$). Values of the two competing rate constants are listed in Table I.

$$\text{Ar}-\overset{\overset{\displaystyle O^*}{\|}}{\text{C}}-\text{CH}_2\text{CH}_2\text{CH}_2\text{R} \xrightarrow{k_H} \text{Ar}-\overset{\overset{\displaystyle OH}{|}}{\text{C}}-\text{CH}_2\text{CH}_2\text{CHR}$$

$$\downarrow k_d \qquad\qquad\qquad \text{pyridine} \downarrow 100\%$$

$$\text{ground state} \qquad\qquad\qquad \text{products}$$

It is difficult to interpret the k_d values, since they include impurity quenching, self-quenching,[13] and solvent quenching.[11b,14] The former two are definitely important for the three ketones which showed concentration-dependent quantum yields. In the case of the 3-methyl- and 3,5-dimethylvalerophenones, however, the large k_d values are puzzling, since quantum yields for these ketones were concentration independent. We surmise that a small fraction of the diradicals may cyclize to products which can revert thermally to reactant ketone.[4] Whatever the cause for the anomaly, the k_H values for these two ketones can be no more than 15% higher than those listed.