Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances, and interatomic angles for the furodysinin hydroperoxide 3 (4 pages). Ordering information is given on any current masthead page.

Solvolysis in Mixed Solvents with Complementary Electrophilic and Nucleophilic Properties. Hexafluoro-2-propanol and 1,3-Propanedithiol

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Solvolytic rates for alkyl tosylates and brosylates were determined for various binary compositions of hexafluoro-2-propanol (HFIP) and 1,3-propanedithiol (PDT). N_{OTs} and Y_{OTs} values were determined by using the Bentley–Schleyer approach. Solvent ionizing power dropped off sharply as PDT replaced HFIP in the mixtures, and a Y_{OTs} value of −4.7 was estimated for pure PDT. A plot of N_{OTs} vs. molar composition of HFIP was nonlinear with solvent nucleophilicity dropping off at high HFIP concentrations. Nevertheless, HFIP–PDT mixtures were, surprisingly, 3 to 4 orders of magnitude more nucleophilic than HFIP–H_2O mixtures although pure PDT is estimated to be only 2.5 orders of magnitude more nucleophilic than pure water. To explain these observations, it is suggested that, at high concentrations of electrophilic solvents, hydrogen bonding to the oxygen or sulfur atom in the more nucleophilic solvent molecules reduces the nucleophilicity of these solvents. The good correlation between rates of a wide variety of substrates in HFIP–PDT and 97% aqueous HFIP suggests that these substrates react by a k_c (or k_Δ) mechanism in these solvents.

The effects that the solvent has on the course of displacement reactions has attracted considerable attention from chemists since Ingold and his colleagues began sorting out the nature of displacement of covalently bound groups.[1,2] Grunwald and Winstein[2,3] made the first major attempt to quantify these effects when they proposed to use eq 1 to correlate these effects for the S_N1 solvolysis of

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

tert-butyl chloride. This two-parameter equation has survived and proven useful despite its simplicity. In recent years there has been growing pressure to improve the correlations.

Grunwald and Winstein originally assumed that *tert*-butyl chloride, the model substrate, ionized without measureable nucleophilic solvent assistance. Hence, they assigned it a substrate sensitivity value, m, of 1.0. Bentley[4] has been the main advocate of the view that failure of some solvents, especially hindered fluorinated alcohols, to be correlated by eq 1 is evidence that *tert*-butyl chloride is experiencing nucleophilic solvent assistance from many hydroxylic solvents. Kevill's work lends support to this view.[5]

Raber and Harris[6] took advantage of the difference in the nucleophilicity of fluorinated and nonfluorinated alcohols in devising their probe for solvent nucleophilicity. However, Abraham, Kamlet, and Taft[7] have taken issue with the importance that Bentley, Harris, and Raber have given solvent nucleophilicity. They point out that their solvatochromatic method[8] suggests that differences in susceptibility to electrophilicity may be the cause of exceptional results.

Clearly, it seems likely that the Grunwald–Winstein treatment fails to satisfactorily deal with susceptibility of *tert*-butyl chloride to either electrophilicity or nucleophilicity. Extended Grunwald–Winstein treatments, which have parameters for ionizing power (or electrophilicity?) and nucleophilicity, have been proposed.[3,9,10] However, because of different susceptibilities to electrophilicity by the leaving group, comparisons with the same leaving group are required.[11] Despite this drawback and some failures in special cases,[12] the four-parameter approach of Bentley and Schleyer,[9] eq 2, is useful in evaluating solvent properties.

$$\log (k/k_0) = mY + lN \qquad (2)$$

Kamlet and Taft's multiparameter approach, eq 3,[7,8] is

$$\log (k/k_0) = h\, \delta_H{}^2/100 + s\pi^* + a\alpha + b\beta \qquad (3)$$

the most sophisticated approach currently undergoing scrutiny. Despite the enthusiasm for the solvatochromatic

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Table I. Solvolysis of Alkyl and Cycloalkyl Brosylates and Tosylates in 95/5 HFIP–PDT (mol/mol)[a]

structure	T, °C	$10^4 k$, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
MeOTs	25.0	0.0248[b]	15.6	-31.9
	50.0	0.206[b]		
	70.1	0.881 ± 0.012		
	75.7	1.37 ± 0.02		
	90.8	3.57 ± 0.06		
	99.4	5.84 ± 0.06		
EtOTs	25.0	0.0319[b]	18.5	-21.6
	50.0	0.387 ± 0.030		
	75.0	3.30 ± 0.10		
2-PrOBs	25.0	0.0601[b]	15.1	-31.8
	40.0	0.203 ± 0.008		
	50.0	0.508 ± 0.020		
	75.0	2.62 ± 0.20		
	100.0	12.7 ± 0.70		
2-BuOBs	25.0	0.848 ± 0.005	10.4	-42.7
	50.3	2.25 ± 0.12		
	75.1	12.6 ± 0.20		
2-BuOTs	25.0	0.378 ± 0.025	9.4	-47.5
	40.0	0.711 ± 0.002		
	50.0	1.22 ± 0.11		
	75.0	4.18 ± 0.03		
3-pentyl-OBs	25.0	1.46 ± 0.20	18.3	-14.7
	50.0	17.3 ± 0.04		
3-Me-2-BuOTs	25.0	2.73 ± 0.08	16.2	-20.4
	50.0	24.6 ± 0.70		
3,3-Me$_2$-2-BuOBs	1.0	1.41 ± 0.04	20.1	-2.57
	25.0	30.1 ± 0.90		
cyclopentyl-OTs	25.0	1.93 ± 0.18	18.2	-14.5
	50.0	22.5 ± 1.1		
2-adamantyl-OBs	25.0	1.37 ± 0.07	17.6	-17.3
	50.0	14.7 ± 1.4		

[a] All solutions contained ca. 0.003 M 2,6-lutidine. [b] Extrapolated from rates determined at other temperatures.

approach by Kamlet, Taft, and their collaborators, there are critics[11a] who are not yet convinced that the method will work for correlation of solvolytic data. Until it has been evaluated thoroughly, any conclusion is unjustified. A severe deterrent to the use and acceptance of the solvatochromic method lies in the very small range of solvents, usable for solvolytic studies, for which parameters are known. Kamlet and Taft are aware that the method cannot give statistically valid results unless several solvents, bearing on the importance of the parameters, are evaluated.[13]
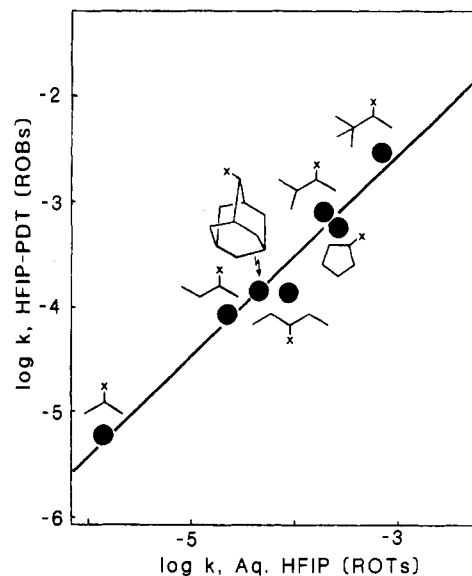
In order to facilitate evaluation of medium effects in displacement processes, we have begun to study protic solvents not ordinarily included in solvolytic studies. In the present article, we report studies of binary mixtures of two very different solvents—one a highly electrophilic but poorly nucleophilic solvent, hexafluoro-2-propanol (HFIP), and the other a poorly electrophilic but highly nucleophilic solvent, 1,3-propanedithiol (PDT).

Results and Discussion

At the outset we hoped to study reactions in pure thiols. However, rates for solvolytic reactions of the common alkyl substrates in simple thiol solvents could not be obtained by using our standard procedures. For example, conductivity in such solutions was found to be low and reactions, monitored by GC analysis, were slow.[14] Assuming that

Figure 1. Plot of the logarithm of pseudo-first-order rates of selected alkyl tosylates in 97/3 HFIP–H$_2$O (w/w) vs. those in 95/5 HFIP–PDT (mol/mol).

the slow rates resulted from a lack of electrophilic capacity of the thiols, we added the electrophilic solvent HFIP and found greatly accelerated rates. HFIP is known for its high electrophilicity and low nucleophilicity.[15] We arbitrarily chose a 95/5 (mol/mol) HFIP–PDT mixture for study of a wide variety of structural types. In Table I are the rates and activation parameters for a sampling of alkyl tosylates and brosylates.

On the whole, the activation parameters for the lower members of the alkyl series seem a little odd. We attempted to establish the validity of these values by running rates over a wide temperature range for 2-propyl brosylate, 2-butyl brosylate, and 2-butyl tosylate. Only a slight curvature results in the plots of log k vs. $1/T$. Activation parameters for 2-butyl brosylate calculated for the two lower temperatures are $\Delta H^{\ddagger}$ = 7.21 kcal/mol, $\Delta S^{\ddagger}$ = -44.4 eu. We have no explanation for the odd activation parameters.

Schleyer and his co-workers have measured rate constants for a variety of substrates in 97/3 HFIP–H$_2$O (w/w) mixtures.[15] Figure 1 shows log k values[16] for reactions of a variety of tosylates in 97/3 HFIP–H$_2$O (w/w)[15,16] vs. log k values for the brosylates of the same structures in 95/5 HFIP–PDT (mol/mol). The correlation is excellent, suggesting no major mechanistic change. We will comment further on the meaning of this correlation and compare rates in the two solvents after we discuss solvent properties below.

In order to determine the properties of HFIP–PDT mixtures and to estimate nucleophilic and electrophilic properties of pure thiols, we adopted the method of Bentley and Schleyer, eq 2.[9] In Table II are rate constants of methyl tosylate at 50 °C and 2-adamantyl tosylate at 25 °C in various compositions of HFIP/PDT. Calculated Y_{OTs} values are found to correlate with the molar solvent composition in the range from 90% to 100% HFIP (r = 0.979), Figure 2. Thus Y_{OTs} values have been extrapolated

(13) Kamlet, M. J., personal communication, November, 1984.

(14) In order to have a boiling point high enough to maintain a tolerable laboratory environment, we explored use of 1-heptanethiol and 1,3-propanedithiol. Although we were not successful in achieving suitable rates in either of these pure solvents (McManus, S. P.; Chandler, D., unpublished results), the experience proved useful in pointing to the need for better handling techniques for the noxious thiols! We chose to avoid any kinetic method which required routine sampling, e.g., GC or HPLC.

(15) Schadt, F. L.; Schleyer, P. v. R.; Bentley, T. W. *Tetrahedron Lett.* **1974**, 2335. Schleyer, P. v. R.; Shoer, L, unpublished results. Schleyer, P. v. R., personal communication.

(16) Rates for the 3-methyl-2-butyl and 3,3-dimethyl-2-butyl tosylates in 97% aqueous HFIP (w/w) were run in our laboratory. At 25 °C, k_1 values, respectively, are 2.14 × 10^{-4} and 7.72 × 10^{-4}. McManus, S. P., unpublished results. These tosylate rates were multiplied by a factor of 3 to get extrapolated brosylate rates.

Table II. Pseudo-First-Order Rate Constants for Methyl Tosylate (at 50 °C) and 2-Adamantyl Tosylate (at 25 °C) in HFIP–PDT Binary Mixtures[a]

solvent (molar %HFIP)	$10^5 k$ MeOTs	$10^5 k$ 2-AdOTs	N_{OTs}	Y_{OTs}
50.0	8.28 ± 0.03		0.70	-0.45[b]
70.0	8.23 ± 0.01		0.19	1.25[b]
75.0	7.53 ± 0.18		0.02	1.68[b]
84.7	6.40 ± 0.02		-0.30	2.51[b]
90.0	3.90 ± 0.14	2.16 ± 0.08	-0.64	2.95[b]
92.5	2.95[c]	4.04[c]	-0.85	3.23
95.0	2.06[d]	4.46 ± 0.15	-1.02	3.27
97.0		10.6 ± 0.2		3.65
98.5		11.3 ± 0.1		3.67
100.0		15.7[e]		3.82

[a] Reaction solutions are ca. 0.001 M in substrate and 0.003 M in 2,6-lutidine. [b] Extrapolated from the linear relationship of molar %HFIP vs. Y_{OTs} for the solvent mixtures containing 90–100% HFIP ($r = 0.979$). [c] One determination at this solvent composition. [d] See Table I. [e] Bentley et al. (ref 17) report 1.47 ± 0.02 × 10^{-4} s^{-1} using a spectrophotometric procedure and 1.57 ± 0.09 × 10^{-4} s^{-1} by conductimetric methods. With a single conductimetric determination, we determined the rate to be 1.72 × 10^{-4} s^{-1}; therefore, we have used the middle value here.
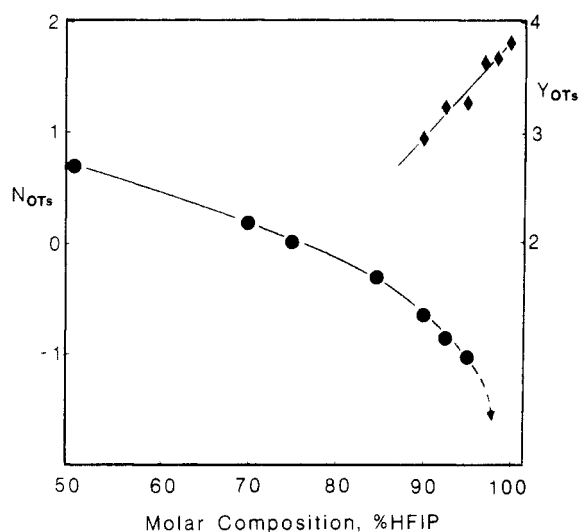
Figure 2. Plots of N_{OTs} and Y_{OTs} vs. % composition of HFIP–PDT.

to other compositions evaluated, Table II. Assuming an m value for MeOTs = 0.3 and its sensitivity to nucleophilicity, l, is 1.0,[9] N_{OTs} values for a range of HFIP–PDT compositions have been calculated, Table II. When viewed along with the extensive list of hydroxylic solvents compiled by Bentley and Schleyer,[9,17] HFIP–PDT mixtures show some unusual properties. Comparing 95/5 HFIP–PDT (mol/mol) with 97/3 HFIP–H₂O (w/w), which is 77.6/22.4 (mol/mol), the aqueous solvent is slightly more highly ionizing (Y_{OTs} = 3.61 compared to 3.27) but, suprisingly, the HFIP–PDT mixture is considerably more nucelophilic (N_{OTs} = -1.02 compared to -4.27 for the aqueous solvent). We will comment further on this below.

Among protic solvents, highly electrophilic solvents are generally poor nucleophiles and poorly electrophilic solvents are good nucleophiles. For example, the most nucleophilic solvents listed by Bentley and Schleyer[9,17] are 2-propanol (N_{OTs} = 0.2, Y_{OTs} = -2.83) and 90% aqueous ethanol (N_{OTs} = 0.01, Y_{OTs} = -0.58), while the most highly ionizing are FSO₃H (N_{OTs} = ca. -4, Y_{OTs} = ca. 17) and CF₃CO₂H (N_{OTs} = -5.56, Y_{OTs} = 4.57). The 50/50

HFIP–PDT mixture has a higher nucleophilicity (N_{OTs} = 0.7) than any of these, and the ionizing power of the HFIP–PDT mixtures drops off rapidly as PDT replaces HFIP. Thus the 50/50 solvent composition has a Y_{OTs} value between that of 80 and 90% aqueous ethanol. By extrapolation of the apparently linear relationship between Y_{OTs} and percent composition (Figure 2) to 100% PDT, the Y_{OTs} value for pure PDT is estimated to be -4.7. This would suggest that PDT may be more poorly ionizing than *tert*-butyl alcohol (Y_{OTs} = -3.74[17]) or any other protic solvent that has been studied, a conclusion that is reasonable considering the relatively poor hydrogen bond donor ability of thiols.

Unlike the linear correlation between Y_{OTs} and HFIP–PDT composition (Figure 2), the relationship between N_{OTs} and molar composition is not linear over the entire range (Figure 2). This may be attributed to hydrogen bonding of HFIP to PDT causing the latter to appear less nucleophilic. A similar explanation has been advanced recently to explain why mustard derivatives give slower than predicted rates in highly electrophilic solvents.[12,18] Importantly, since ROH is a better H-bond acceptor than RSH,[8] hydrogen bonding may also explain why 97/3 HFIP–H₂O is 3 orders of magnitude less nucleophilic than 95/5 HFIP–PDT.

Since an initial goal was to determine the nucleophilicity of pure thiols, it is of interest to get an estimate of N for pure PDT. This is possible by using an admittedly long and perhaps flawed extrapolation. Within our subjective framework, we note that the composition vs. N_{OTs} plot does become linear below ca. 85% HFIP. Assuming this linear relationship continues, it is possible to estimate the nucleophilicity of pure PDT. Using the linear part of the composition vs. N_{OTs} plot (e.g., 50–70% HFIP, Figure 2), we extrapolate the N_{OTs} value of pure PDT to be 1.98. In general, then, pure PDT is about 2 orders of magnitude more nucleophilic than alcohols and about 2.5 orders of magnitude more nucleophilic than pure water. When taken with the discussion in the previous paragraph, we can estimate that water is becoming relatively less nucleophilic in the presence of HFIP. This tends to support our suggestion of stronger hydrogen bonding to water than the thiol.

Let us now return to our plot of rates in aqueous HFIP vs. those in HFIP–PDT, Figure 1. If reliable ROTs/ROBs rate ratios were available we would have compared tosylates in the two solvents. However, the literature reveals that these ratios range from around to 2 to 6 depending on solvent and substrate type.[19,20] We measured the ratio in 95/5 HFIP–PDT for the 2-butyl and 2-adamantyl substrates, Tables I and II. The ratio at 25 °C for 2-butyl, normally a k_s substrate,[1a] is 2.24 while that for 2-adamantyl, a k_c substrate,[1a] is 3.07. These ratios are similar to those normally found for solvolysis in electrophilic solvents for limiting substrates.[19,20] Applying the ROBs/ROTs ratio of 3 to the rates of tosylates in HFIP–H₂O, we calculate that rates of the brosylates in the two solvents are about equal; e.g., log k = -5.52 (HFIP–H₂O) vs. -5.46 (HFIP–PDT) on the low end and log k = -2.52

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(17) Bentley, T. W.; Carter, G. E. *J. Org. Chem.* **1983**, *48*, 579.

(HFIP–H$_2$O) vs. –2.60 (HFIP–PDT) on the high end of the reactivity scale. This is not surprising if reactivity is controlled predominantly by the solvent's ionizing power term, Y_{OTs}, as these solvents have similar Y_{OTs} values. What is surprising, however, is the good correlation of all substrates even though in solvents of moderate nucleophilicity and ionizing power (e.g., aqueous alcohols) they represent k_s, k_c, and k_Δ types.[1a] For example, because the nucleophilicity of HFIP–PDT is 3 orders of magnitude greater than that of HFIP–H$_2$O (N_{OTs} = –1.02 and –4.27, respectively), one would expect the k_s substrates to react faster in HFIP–PDT. It thus appears that, unlike MeOTs, the model k_s substrate used to define the N values, solvent nucleophilicity may be kinetically unimportant for the secondary substrates in these highly electrophilic solvents. However, we cannot rule out the contribution of steric effects on solvent nucleophilicity.[10c,21]

In summary, we have studied various HFIP–PDT compositions, finding that thiols indeed are highly nucleophilic solvents. However, with their poor electrophilicity, solvolytic rates in pure thiols are very low. By mixing them with an electrophilic cosolvent like HFIP, high reaction rates may be obtained. Using the Bentley–Schleyer method of determining solvent ionizing power and nucleophilicity, the HFIP–PDT mixtures were characterized. The low nucleophilicity of HFIP–H$_2$O and the nonlinearity of our N_{OTs} vs. molar composition plot was attributed to hydrogen bonding to the more nucleophilic oxygen or sulfur atom by the electrophilic cosolvent (or by either solvent in HFIP–H$_2$O). Secondary substrates, in both 95/5 HFIP–PDT (mol/mol) and 97/3 HFIP–H$_2$O (w/w), are suggested to react by k_c or k_Δ mechanisms. As more of the nucleophilic cosolvent is added (i.e., either PDT or H$_2$O,

respectively), other evidence would suggest that the normally k_s substrates should become k_s in these binary mixtures.

Experimental Section

Chemicals. Methyl tosylate, obtained commercially (Eastman and Aldrich), was recrystallized. All other tosylates and brosylates were prepared by the standard pyridine method[22] and purified by repeated recrystallization at –70 °C from low boiling petroleum ether. All tosylates and brosylates were stored at –10 °C. All of the sulfonate esters were previously prepared and characterized, hence structures were verified by comparison of melting points, where appropriate, with literature values and by characteristic IR and NMR spectra. Solvents were dried over 3A molecular sieves, purified by distillation, and stored in a desicator.

Kinetics. Rates were determined conductimetrically as previously described[23] but using conductimetric cells with pressure seals (Teflon) to prevent solvent loss. Each kinetic sample contained about 10 mL of solvent ca. 10^{-3} M in substrate and ca. 3 × 10^{-3} M in 2,6-lutidine.

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Comparison of Substituent Constants for Correlation of Nuclear Magnetic Resonance Absorptions of β-Carbon Atoms in Ortho-Substituted Styrenes

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The nuclear magnetic resonance absorptions of β-carbon atoms in ten series of ortho-substituted styrenes have been studied. Each series included the following substituents: methoxyl, methyl, hydrogen, fluoro, chloro, bromo, and nitro. A set of substituent constants based on the present data corresponds fairly well with previously published sets. Dual substituent parameter analyses that neglect steric factors give significantly poorer correlations. Both the Charton and the Fujita–Nishioka three-parameter treatments that incorporate a steric factor give excellent correlations. The magnitude of the steric contribution in the correlations agrees well with expectation based on the total steric environment.

The early literature contains reports that ortho-substituted benzenes show unusual chemical behavior, which led to the belief that ortho substituents might exert both steric and electrical effects at a reaction center.[1] Accordingly, Hammett felt that the usual type of correlation between reactivity and substituent constant might be precluded because such correlations for meta and para substituents presuppose an absence or constancy of steric

[†]Based in part on work described in the M.S. Thesis of James L. Horton, Memphis State University, August, 1982.

(1) Charton, M. *Prog. Phys. Org. Chem.* 1971, *8*, 235–317. This article summarizes earlier work in the field.