index i is given only once, initially or after a backslash, followed by pairs of solvent j and z values, with leading and trailing zeros omitted to save space, in these computer-generated and computer-readable tables.

See Experimental Section of the following paper[40] for details of hardware and software used.

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Solvent Effects on Chemical Reactivity. Evaluation of Anion and Cation Solvation Components

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Abstract: Free energy changes due to solvent are fitted for 61 solvents and 77 reactions by $aA + bB + c$, where A (anion-solvating tendency) and B (cation-solvating tendency) depend on only the solvent and a, b, and c depend on solely the reaction. The input data are based on rate constants, product ratios, equilibrium constants, and electronic, IR, ESR, and NMR spectra. All 353 (=(2 × 61) + (3 × 77)) A, B, a, b, and c constants are evaluated by nonlinear least squares by using equal statistical weighting of 1080 data, the four trivial scale-setting subsidiary conditions $A = B = 0$ for *n*-heptane and $A = B = 1$ for water, and the two critical subsidiary conditions $A = 0$ for hexamethylphosphoric triamide and $B = 0$ for trifluoroacetic acid. There is no correlation between A and B values. The precision (standard deviation) is listed for each of the 353 constants and also the correlation coefficient for each solvent and for each reaction. The overall correlation coefficient between input data and predictions is 0.991; no individual solvent is below 0.970 and no reaction below 0.975. Benzene has $A = 0.15$, $B = 0.59$, which makes it more polar than CCl_4 but less polar than acetone. Solvolysis of *tert*-butyl chloride has $a = 7.4$, $b = 5.6$, but solvolysis of triphenylmethyl fluoride is more sensitive to the solvent's ability to solvate anions ($a = 14.9$, $b = 1.8$), while EtI + Et_3N favors cation solvators relatively more ($a = 0.9$, $b = 4.4$). The reaction correlation coefficient is below 0.975 for many other reactions owing to a change in the mechanism or process under observation at some point within the range of solvents studied, with this point often becoming evident upon scrutiny of the individual deviations for each solvent.

Attempted Solvent Effect Predictions Based on One Constant per Solvent

Solvent effect equations have usually involved only a single solvent vector **A**, i.e., only a single string of solvent constants A_j, one for each solvent j, in a simple linear free energy relationship (eq 1) for predicted solvent effects p_{ij}. Here any lower case a_i

$$p_{ij} = a_i A_j + c_i \tag{1}$$

represents the sensitivity of reaction i to solvent change and c_i is the predicted value for the reference solvent j_0 (for which $A_j = 0$).

In 1948, Grunwald and Winstein[2] evaluated A_j values, which they called Y or "solvent ionizing power", for various solvents and solvent mixtures from logarithms of first-order rate constants for solvolysis of *tert*-butyl chloride at 25 °C ($Y = \log k_1(j) - \log k_1(80\%\ \text{ethanol})$). Numerous alternative A sets appeared subsequently, e.g., Kosower's Z and Dimroth's E_T derived from spectral absorption frequencies and Berson's Ω from a product ratio.[3-5] Each investigator plotted energy changes in other reactions vs. his A values. These plots are roughly linear, more nearly linear the closer the mechanism or nature of the reaction plotted is to that of the defining reaction. These different A sets also correlate moderately well with one another. In Reichardt's superb review[6] of work on solvent effects through 1977, all pre-1978 equations and parameters for predicting solvent effects are clearly presented and critically assessed in his final chapter[7] and all pertinent references are cited.

Use of eq 1 presupposes that only one solvent property significantly affects reactivity, or, if two independent properties are influential (as assumed in eq 2), that a_i/b_i (the ratio of sensitivities to the two properties or vectors) is nearly constant for reactions to which eq 1 applies. Evidently the blend or mix of a and b is comparable for the A sets mentioned above. In the light of the present study, it now appears that a_i/b_i is 1.3 for Y, 5.4 for Z, 6.8 for E_T, and 3.9 for Ω. This variation is minor compared to the range from −240 to +67 that we find for other reactions among the 77 listed in Tables I and II.

Tables I and II list 77 reactions and 1080 data suitable for testing various procedures.[8-59] The 77 reactions comprise 32 series

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(1) (a) Chose the six subsidiary conditions. (b) Developed and executed computer programs. (c) Office of Naval Research from 1947 to 1979. Guest of M.I.T. Searched literature for accurate data. (d) Present address: Istituto di Chimica Organica, Università di Perugia. Measured reactions 45-47.

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Table I. Reactions Used To Test Eq 1 and 2

i^a	data type^b	reactant^c	T^d	sign & unit^e	p^f
1	$\Delta \log k_1$	MeBr	50	+	8
2		MeOTs	50	+	9
3		BuBr	75	+	10
4		$PhCH_2Cl$	50	+	10
5		Me_2CHOTs	25	+	11
6		*cyclo*-C_5H_9OTs	25	+	12
7		*cyclo*-$C_6H_{11}OTs$	25	+	12
8		*endo*-$C_7H_{11}OTs$	25	+	12
9		*exo*-$C_7H_{11}OTs$	25	+	12
10		Ph_2CHCl	25	+	10
11		2-AdOTs	25	+	13
12		Me_3CCl, *Y*	25	+	14
13		Me_3CBr	25	+	15
14		$PhCMe_2O_2COPh$	50	+	16
15		Ph_3CF	25	+	17
16		Ph_3COAc	25	+	18
17	$\Delta \log k_2$	MeI + $(EtCH_2)_3N$	20	+	19
18		MeI + $PhNMe_2$	30	+	20
19		MeI + 3-$ClPhNMe_2$	30	+	20
20		MeI + 4-$ClPhNMe_2$	30	+	20
21		MeI + 3-$MePhNMe_2$	30	+	20
22		MeI + 4-$MeOPhNMe_2$	30	+	20
23		EtI + Et_3N	25	+	21
24		$EtO_2CCH_2Br + Et_3N$	20	+	22
25		$EtO_2CCH_2I + Et_3N$	20	+	22
26		4-$O_2NPhF + Et_4N^+N_3^-$	25	–	23
27		$PhSO_2Cl + PhNH_2$	25	+	24
28		$ClSO_2NCO$ + hexene	25	+	25
29		TCNE + 4-MeO-styrene	–	+	26
30		Br_2 + 1-pentene	25	+	27
31		$Br_2 + Me_4Sn$	20	+	28
32	$\Delta \log k_d$	2-$PhSPhCO_3CMe_3$	25	+	29
33	$\Delta \log Q$	Berson Ω	30	+	30
34		sulfoxide rearr	25	–	31
35	$\Delta \log K$	$PhCO_2H$	25	+	32
36		2-O_2NPhOH	–	+	33
37		picramic acid	–	+	33
38		*o*-vanillin	–	+	34
39		5-methylfurfural	–	+	34
40		1-NO-2-naphthol	–	+	35
41		2-NO-1-naphthol	–	+	35
42	ΔG^0	$Et_4N^+I^-$	25	– kcal	36
43	UV	Kosower *Z*	25	+ kcal	37
44		MPI	–	+ kcal	38
45		3-$MeOC_5H_4N^+O^-$ (1)	25	+ kcal	39
46		3-$MeOC_5H_4N^+O^-$ (2)	25	+ kcal	39
47		3-$MeOC_5H_4N^+O^-$ (3)	25	+ kcal	39
48		$PhNO_2$	–	– 10^6 m^{-1}	40
49		4-$MeOPhNO_2$	–	– 10^5 m^{-1}	41
50		4-Et_2NPhNO_2	–	– 10^5 m^{-1}	41
51		Ph_2CO	–	+ 10^5 m^{-1}	42
52		pyrimidine	–	+ 10^5 m^{-1}	43
53		pyridazine	–	+ 10^5 m^{-1}	43
54		pyrroline oxide	–	+ 10^5 m^{-1}	44
55		Fe imine	25	+ 10^5 m^{-1}	45
56		oximate	–	+ kcal	46
57		sulfoxide	–	+ 10^5 m^{-1}	47
58	VIS	Dimroth E_T30	25	+ kcal	48
59		Dimroth E_T26	25	+ kcal	49
60	UV	Brooker χ_R	–	– kcal	50
61		Davis *A*	–	+10^5 m^{-1}	51
62		Davis *B*	–	+ 10^5 m^{-1}	51
63	FLUOR	Davis E_{CT}	–	– kcal	52
64	IR	$HCONMe_2$	–	– cm^{-1}	53
65		$POCl_3$	–	– cm^{-1}	54
66		Me_2CHCH_2Cl, trans	–	– cm^{-1}	55
67		Me_2HPO, band 1	–	– cm^{-1}	54
68	ESR	$(Me_3C)_2NO$, N	rt	+ gauss	56
69		piperidyloxy, N	rt	+ gauss	56
70		pyrrolinyloxy, N	rt	+ gauss	56
71		4-AcC_5H_4NMe, 2-H	–	– gauss	57
72		4-AcC_5H_4NMe, 3-H	–	+ gauss	57
73		4-AcC_5H_4NMe, 5-H	–	+ gauss	57
74		4-AcC_5H_4NMe, 6-H	–	–gauss	57
75		4-AcC_5H_4NMe, Ac-H	–	+ gauss	57
76	NMR	2-F-picoline, F	rt	– δ(ppm)	58
77		Et_3PO, P	–	– 0.426 δ	59

[a] See footnote *c* for abbreviations. 28 is 2-ethyl-1-hexene; 33 is log ratio of endo to exo Diels–Alder products from methyl acrylate and cyclopentadiene; 34 is log ratio of a sulfenate, 2-$O_2NPhSOCH_2CH{=}CH_2$, to its sulfoxide isomer; 37 is 2-H_2N-4,6-$(O_2N)_2PhOH$; 38 is 2-HO-3-MeOPhCHO; 43 is 1-ethyl-4-(methoxycarbonyl)pyridinium iodide; 44 is 1-((methacryloyl)oxy)ethyl-4-(ethoxycarbonyl)pyridinium iodide; 45–47 are 3-methoxypyridine *N*-oxide; 54 is 5,5-dimethylpyrroline 1-oxide (contains $C{=}N^+{-}O^-$); 55 is bis[*N*-(2-pyridylmethylene)-3,4-dimethylaniline]bis(cyanoiron); 56 is $CH_3N^+C_5H_4$-4-$C(CN){=}NO^-$, lower *E* band; 57 is $PhC(NMe_2){=}S{=}O$; 58 is a betaine, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide; 59 is 2,6-di-*tert*-butyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide; 60 is a $C_{30}H_{37}N_3O_2S$ merocyanine dye containing $R_2N(C{=}C)_5C{=}O$; 61 is 1,3,5-$(O_2N)_3Ph$ + $(n\text{-}C_6H_{13})_4N^+I^-$; 62 is tetrachloroquinone + $Bu_4N^+Br^-$; 63 is tetrachlorophthalic anhydride + Me_6Ph; 69 is 4-amino-2,2,6,6-tetramethylpiperid-1-yloxy radical; 70 is 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy radical; 77 is Gutmann acceptor number AN (see also ref 6, pp 18, 19, 249, 250). [b] $\Delta \log k_1$ = log (base 10) of relative first-order rate constant for solvolysis; $\Delta \log k_2$ = log of relative second-order rate constant; $\Delta \log k_d$ = log of relative first-order rate constant for thermal decomposition to free radicals; $\Delta \log Q$ = change in log of ratio of isomeric products; $\Delta \log K$ = log of equilibrium constant for distribution between solvents; ΔG^0 = free energy of transfer from reference solvent; VIS or UV = electronic absorption maximum; FLUOR = fluorescence emission; IR = infrared absorption; ESR = electron spin resonance hyperfine splitting constant; NMR = nuclear magnetic resonance chemical shift. [c] Ac = acetyl; Ad = adamantyl; Bu = *n*-butyl; Et = ethyl; Me = methyl; OBs = *p*-bromobenzenesulfonate; OTs = *p*-toluenesulfonate; Ph = phenyl or –benzene; TCNE = tetracyanoethylene; C_6H_{11} or $-C_6H_{10}-$ = cyclohexyl; C_7H_{11} = norbornyl. See Table VI for number of solvents, nj_i. See input data. [d] Temperature in °C; rt = room temperature. If "–" is listed, literature reference[f] does not specify it, but we assume that it was between 20 and 75 °C. [e] A "+" sign indicates that the log *k*, log *Q*, log *K*, ΔG^0, or spectral energy, frequency, or field shift is an *increase* relative to the reference solvent, which has the lowest literature[f] value for that *i* and hence has the smaller value (0.0) in Table II. A "–" sign indicates a *decrease* relative to the reference solvent, which has the largest literature value for that *i* and hence has the smallest value (0.0) in Table II. Reactions 1–41 have dimensionless data. Units for reactions 42–77 are the same as or integral power-of-10 multiples of those used in literature references[f] and refer to 1 mol of reaction (transfer, excitation, or emission). For other units, 1 kcal = 350 cm^{-1} = 3.5×10^4 m^{-1} = 4.184 kJ. [f] Page or pages from which data were taken are cited in these literature references, except for 39, which refers to reactions (*i* = 45–47) measured in this work.

of rates, 2 product ratios, 8 equilibria (for distributions between solvents), 21 electronic spectra, 4 IR, 8 ESR, and 2 NMR series. These and many other rates and electronic spectra are extremely solvent sensitive. On the other hand, many NMR shifts with

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Table II. Observed Solvent Effects, 1080 Data for 77 Reactions and 61 Solvents, Used as Input for ROSE, LOVE, and DOVE Analyses[a]

```
1 4 .0 15 1.03 31 6.44 32 5.36 37 5.32 41 3.63 55 2.46 57 1.78 59 2.19 \ 2 4 2.764 7 3.87 11 .0 14 1.646 15 3.661 55 4.985 57 4.191
59 4.489 \ 3 4 .0 7 .78 15 .44 31 3.86 32 3.26 37 3.49 41 .0 46 2.96 56 .93 57 1.14 58 1.41 \ 4 7 1.21 15 .62 31 4.17 32 3.23 37
4.22 41 .0 46 3.82 57 1.47 59 2.21 \ 5 4 2.488 7 1.183 11 2.507 14 .0 15 .567 55 3.715 57 1.579 58 2.055 59 2.278 \ 6 4 2.656 7 .776
11 3.219 14 .0 15 .211 55 3.925 57 1.247 \ 7 4 2.929 7 .542 11 3.772 14 .029 15 .0 55 4.235 57 1.216 \ 8 4 3.286 7 .816 11 4.427 14
.725 15 .0 55 4.232 57 1.406 \ 9 4 4.066 7 .9 11 5.028 14 .725 15 .0 55 4.987 57 1.722 \ 10 14 1.58 31 .71 32 .0 37 3.79 46 3.07 56
3.87 57 3.94 60 2.56 61 3.21 \ 11 4 4.789 11 6.32 14 1.137 15 .0 57 1.746 58 2.667 59 3.038 \ 12 4 5.314 5 3.864 7 2.17 14 1.585 15
1.227 21 .53 29 .0 55 6.753 56 2.54 57 3.26 58 4.384 59 4.915 60 2.587 61 3.39 \ 13 4 3.5 7 1.06 14 .0 15 .17 57 2.08 58 3.1 60 1.56
61 2.23 \ 14 6 .9693 7 1.952 14 2.4738 15 1.6069 27 1.3296 29 .6353 35 .4534 38 .0 \ 15 14 3.554 15 .062 56 1.902 57 1.792 60 .0 61
.578 \ 16 14 2.736 15 .514 56 1.587 57 1.561 58 2.118 60 .0 \ 17 1 1.3 2 3.264 3 3.597 6 4.191 7 2.26 8 1.55 9 .928 10 2.114 12
3.822 13 3.73 15 2.13 18 3.326 19 3.928 20 2.02 22 3.141 23 2.61 24 2.49 25 2.72 27 1.81 28 1.23 33 3.1 34 3. 35 3.831 36 2.41 38
3.354 39 .0 43 3.741 44 2.13 45 3.1 49 3.773 51 1.866 52 1.89 54 .75 \ 18 7 2.6684 8 1.497 12 4.0129 15 2.5018 18 3.716 21 2.3599 23
3.0171 25 3.0454 33 2.9243 34 2.8028 35 3.7959 36 2.5484 39 .0 44 2.3335 \ 19 7 3.2553 8 1.6368 12 4.5097 15 3.0557 18 4.1875 21
2.8594 23 3.4357 25 3.4094 33 3.1996 34 3.062 35 4.1913 36 2.8958 39 .0 44 2.6813 \ 20 7 3.2192 8 1.7147 12 4.4753 15 3.0188 18
4.1856 21 2.8696 23 3.4456 25 3.4178 33 3.2376 34 3.1068 35 4.2186 36 2.8754 39 .0 44 2.6478 \ 21 7 2.5756 8 1.5094 12 3.9417 15
2.4263 18 3.6369 21 2.2927 23 2.9602 25 2.9602 33 2.8918 34 2.7841 35 3.7414 36 2.4901 39 .0 44 2.2935 \ 22 7 2.3452 8 1.3691 12
3.7446 15 2.273 18 3.4923 21 2.1049 23 2.8293 25 2.8339 33 2.7418 34 2.6173 35 3.6001 36 2.3724 39 .0 44 2.1603 \ 23 1 1.4953 2
3.3486 3 3.773 6 4.392 12 4.226 13 3.844 16 4.811 18 3.686 19 4.204 22 3.468 23 2.938 24 2.761 25 2.9419 28 1.4251 33 3.407 34 3.16
35 4.135 36 2.6 39 .204 40 .0 43 4.052 44 2.3976 49 4.085 \ 24 1 .5441 6 3.3011 12 2.9031 13 2.6128 18 2.3325 22 2.1462 35 2.8129 36
1.4772 39 .0 42 2.1462 43 2.7782 44 1.2553 45 2.1614 49 2.699 52 1.0607 \ 25 1 .6627 6 3.0492 12 2.8195 13 2.5798 18 2.3802 22
2.2253 35 2.7482 36 1.5051 39 .0 42 2.1643 43 2.6627 44 1.3424 45 2.1398 49 2.6434 52 1.1335 \ 26 6 3.799 7 7.238 12 3.332 16 3.31
18 2.388 19 2.852 26 2.293 35 2.852 42 .0 43 2.967 \ 27 7 2.6359 15 2.4866 20 2.3479 24 .6713 27 2.2467 35 .0 \ 28 2 2.3979 3 3.2272
6 3.7958 28 1.4948 34 2.5282 35 3.6989 39 .243 40 .0 44 1.9098 \ 29 3 4.5706 12 4.7979 13 4.4804 24 3.0477 39 .0 \ 30 1 .0 4 8.64 7
5.21 14 3.68 15 3.74 21 3. 25 1.7 29 2.75 55 10.026 \ 31 1 .0 7 5.71 12 4.84 14 4.8 16 6.4 19 5.6 34 2.9 \ 32 7 2.9209 12 2.0109 15
2.3702 16 2.0519 18 1.2831 21 2.1305 29 1.7276 34 1.2521 39 .0 \ 33 6 .235 7 .386 12 .247 13 .155 14 .378 15 .273 18 .156 19 .175 30
.098 32 .15 41 .0 \ 34 1 .0 2 .5642 7 .8765 12 .5532 18 .3228 36 .1553 \ 35 1 .76 13 1.85 34 1.53 36 1.4 39 .37 40 .0 44 1.32 \ 36 1
.5221 2 .9571 13 1.2051 35 1.3131 36 .9311 39 .0561 40 .0 44 .8691 48 .0101 \ 37 1 1.064 2 1.99 13 2.522 33 1.949 35 3.06 36 2.152
39 .146 44 2.06 48 .0 50 2.143 51 2.086 52 2.117 \ 38 1 .866 2 1.769 13 1.822 33 1.446 34 1.468 35 1.769 36 1.337 39 .192 44 1.2 48
.0 50 1.131 52 1.137 \ 39 1 .0 33 .533 34 .549 36 .434 44 .315 50 .282 51 .235 52 .224 \ 40 1 .852 2 1.763 13 1.989 33 1.579 34
1.528 36 1.355 39 .102 44 1.324 48 .0 \ 41 1 .75 2 1.837 13 2. 33 1.486 34 1.458 36 1.243 39 .097 44 1.227 48 .0 \ 42 6 7.7 7 8.9 12
7.5 13 7.3 15 7.6 18 6.6 19 8. 20 7.1 21 6.5 22 5.7 24 3.6 27 6.8 28 .0 29 5.1 33 5.5 34 3.8 35 6.8 36 2. 43 6.8 49 6.2 55 16.4 \ 43
3 6.7 5 25.3 7 25.6 12 13.3 15 21.6 16 13.1 17 27.1 18 7.5 19 10.4 20 20.3 21 18.3 27 19.7 29 13.3 30 1.1 32 6. 33 1.2 34 .0 43 7.
56 26.1 57 26.8 60 22.7 61 25.2 \ 44 5 23.02 7 24.05 12 11.7 15 20.17 18 5.81 19 8.9 20 18.39 21 16.44 22 1.75 25 .0 27 18.07 29
11.02 32 4.15 37 12.53 \ 45 1 1.84 3 3.52 7 6.77 12 3.45 13 3. 15 6.45 16 3.22 19 2.93 24 2.12 25 2.34 28 1.05 30 2.42 36 1.62 41 .7
53 .0 55 8.23 \ 46 1 .0 3 2.56 7 7.86 12 3.12 13 2.28 15 7.04 16 2.46 19 2.28 24 2.18 25 1.81 28 1.63 30 2.18 36 1.17 41 1.26 53
1.36 55 11.39 \ 47 3 1.17 7 6.49 12 2.22 15 6.21 28 .52 53 .0 55 8.81 \ 48 1 .57 2 1.59 15 1.16 39 .2 48 .0 55 2.37 \ 49 1 .75 3
2.06 5 2.66 7 1.52 13 1.95 15 1.42 16 2.61 17 2.36 19 2.26 21 1.37 23 1.52 24 1.52 25 1.42 26 2.26 27 1.42 28 .86 29 1.37 32 2.31 36
1.47 39 .18 40 .0 42 2.41 45 1.9 48 .0 54 .75 55 2.76 \ 50 1 1.01 3 2.75 5 3.99 7 2.55 10 1.95 13 2.65 15 2.23 16 3.41 17 3.61 18
2.49 19 3.05 21 2.2 22 2.43 23 2.1 24 1.97 25 1.94 26 2.96 27 2.2 28 1.19 29 2.1 32 2.93 34 2.33 36 2.11 39 .31 40 .0 41 .57 42 2.96
44 1.84 45 2.4 48 .0 54 .86 55 4.48 \ 51 7 1.31 12 .68 13 .51 15 1.22 16 .51 19 .47 20 1.13 27 1.13 28 .21 39 .0 40 .0 \ 52 1 .14 2
.81 3 .66 7 1.57 12 .66 15 1.31 16 .53 19 .4 20 1.25 21 1.18 23 .34 24 .43 25 .31 26 .4 27 1.15 28 .25 36 .25 39 .0 48 .01 53 .01
\ 53 1 .4 2 1.42 3 1.26 7 2.68 12 1.37 15 2.38 16 1.2 18 1.06 19 1.12 20 2.3 21 2.14 23 .71 24 .87 25 .78 26 1.09 27 2.21 28 .52 36
.67 39 .0 48 .44 53 .04 55 3.85 \ 54 7 2.42 12 1.19 15 2.09 17 2.62 27 1.9 39 .0 55 3.6 \ 55 6 .74 7 1.57 12 .4 15 1.26 16 .31 17
1.67 18 .0 19 .13 20 1.13 21 .99 27 1.06 29 .65 55 2.54 \ 56 3 .0 7 10.8 12 2.2 15 8.4 16 2.5 18 .7 21 6.3 55 16.9 \ 57 1 .0 2 .93 3
.76 5 1.66 7 2.1 12 .89 14 3.13 15 1.83 16 .64 17 2.15 18 .68 19 .64 21 1.74 25 .32 27 1.7 29 1.57 30 .52 32 .44 34 .32 36 .16 37
.81 39 .0 41 .04 55 2.65 57 2.1 58 2.28 59 2.33 \ 58 1 1.6 3 10.2 5 25.7 6 15.4 7 24.61 8 1.7 9 1. 10 5. 12 15.1 13 8.5 15 21.08 16
14.1 17 25.4 18 11.33 19 12.9 20 19.8 21 17.81 22 10.4 23 6.5 24 7.2 25 5.06 26 12.8 27 19.3 28 3.7 29 13. 30 7.3 32 9.37 33 6.6 34
6.6 36 3.6 37 13.4 38 9.9 39 .3 40 .0 41 2.4 43 11.1 44 3. 45 6.3 47 5.75 49 10.4 54 2.5 55 32.2 57 22.84 58 24.08 59 24.7 60 21.27
61 22.44 \ 59 3 4.3 7 17.8 12 8.4 15 13.9 16 6.7 17 18.1 18 4.9 19 6.4 20 12.6 23 2.1 24 2.4 25 1.2 27 12. 30 2.5 32 4.3 34 2. 36 .2
37 6.7 44 .0 47 1.9 \ 60 1 2.2 2 6.7 3 6. 7 7.8 15 7. 16 8.9 17 10.5 19 7.2 20 6.8 21 6.4 22 5.5 23 4.3 24 3.7 26 7.9 27 6.4 28 2.6
32 7. 33 6.3 34 5.7 36 4. 37 9.8 38 6.6 39 .9 40 .0 41 1.6 43 7.6 44 3.7 47 6.2 48 .0 50 3.6 51 3.1 52 3.2 53 .0 54 2.3 \ 61 1 1.05
3 2.35 6 1.85 7 6.55 8 .4 12 2.85 15 6.45 16 2.15 17 7.25 18 .95 20 5.95 21 4.75 23 .85 24 .75 27 5.65 28 .45 29 3.25 33 1.05 36
1.15 44 1.05 45 1.35 49 .65 \ 62 1 .2 3 1.1 6 1.4 7 3.5 8 .4 12 .9 15 3.4 18 .3 20 3.2 21 3.1 23 .35 24 .4 27 3.3 29 1.6 33 .4 36 .0
49 .0 \ 63 1 .057 8 .053 36 .0 39 .097 40 .123 44 .007 54 .015 \ 64 1 9. 2 23. 3 22. 6 21. 7 27. 8 9. 9 7. 12 20. 13 19. 15 28. 25
16. 28 8. 32 19. 36 12. 39 2. 40 .0 41 6. 44 10. 54 6. \ 65 1 6. 2 15. 3 15. 8 8. 9 5. 34 11. 36 9. 39 .0 40 .0 \ 66 6 13. 8 4. 9
2.5 12 12. 18 10.5 24 8.5 25 9.5 28 5. 36 8.5 39 .5 40 .0 \ 67 1 9. 2 27. 6 26. 8 11. 9 8. 12 24. 28 9. 32 20. 36 12. 39 .0 40 .0 44
14. 54 6. \ 68 1 .197 2 .729 3 .618 6 .625 7 1.076 8 .155 12 .532 13 .521 14 1.286 15 .896 16 .558 17 1.23 18 .393 19 .501 21 .839
23 .239 25 .318 27 .884 28 .2 29 .726 30 .29 32 .474 33 .345 34 .338 36 .27 40 .0 44 .213 49 .428 \ 69 1 .185 2 .556 3 .556 6 .639 7
.98 8 .155 12 .542 13 .49 15 .856 16 .552 17 1.079 18 .402 19 .453 21 .825 23 .255 25 .32 27 .819 28 .202 29 .693 30 .306 32 .444 33
.346 34 .344 36 .313 40 .0 44 .242 49 .42 \ 70 1 .224 2 .693 3 .607 6 .698 7 1.102 8 .16 12 .618 13 .536 14 1.194 15 .962 16 .6 17
1.195 18 .451 19 .5 21 .895 23 .292 25 .363 27 .918 28 .239 29 .797 30 .34 32 .519 33 .357 34 .353 36 .275 40 .0 44 .276 49 .461
\ 71 7 1.14 12 .54 16 .72 18 .36 19 .56 23 .22 28 .0 30 .26 36 .14 55 1.6 \ 72 7 1.08 12 .48 16 .56 18 .34 19 .44 23 .18 28 .0 30
.22 36 .08 55 1.55 \ 73 7 1.04 12 .46 16 .55 18 .32 19 .42 23 .16 28 .0 30 .22 36 .1 55 1.48 \ 74 7 1.17 12 .52 16 .72 18 .34 19 .5
23 .2 28 .0 30 .3 36 .18 55 1.72 \ 75 7 2.36 12 .78 16 .87 18 .52 19 .68 23 .24 28 .0 30 .32 36 .22 55 3.67 \ 76 1 .47 2 2.39 3 1.56
7 4.36 8 .36 15 3.83 16 1.1 17 4.4 18 .98 20 3.74 21 3.44 23 .59 24 .9 25 1.07 27 3.63 28 .42 29 2.05 32 1.01 34 .95 35 1.22 36 .47
39 .0 40 .14 43 1.3 44 .36 45 .88 47 .83 57 4.22 \ 77 1 8.6 2 23.1 3 20.4 5 39.8 6 20.5 7 41.3 11 105.3 12 18.9 13 16.7 14 52.9 15
37.1 16 19.3 18 12.5 19 16. 21 33.5 23 8. 25 10.8 26 13.6 28 3.9 30 10.2 32 14.2 35 14.8 36 8.2 40 .0 43 15.5 55 54.8
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[a] Reactions are separated by backslashes. Reaction *i* is followed by each solvent *j* and its datum, with leading and trailing zeros omitted to save space. See Table I for reaction, reference, and sign information for each *i*; see Table III for solvent for each *j*.

solvent appear to have only marginal accuracy and precision. We have omitted a few data that were based on secondary standards (i.e., that used another reaction and an assumed relationship between the reactions) or that were obtained by extrapolation from other temperatures or solvents or by a different group of investigators, or in solvents like CH_3CN or CH_3NO_2 where purity and previous treatment could be important but were not adequately specified in the experimental part. However, we have omitted relatively few such data compared to other investigators in this area.[60]

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(60) As a typical example, in Table II we retain E_T data for triethylamine, methyl ethyl ketone, nitromethane, ethyl ether, hexane, and cyclohexane, all omitted by Kamlet et al. (Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1725), property (1) in their Table 2. We use 47 E_T data whereas they use only 31.

Two procedures were tested using eq 1. Our minimum standard for an acceptable fit is an overall correlation coefficient C of 0.965, because such agreement between observed data (log k, log K, or ΔG) and predicted data is attainable in other areas of physical organic chemistry, e.g., in Brønsted-law catalysis or in substituent effects.[61,62]

First, the 1080 data were correlated vs. one of the A sets by our simple linear least-squares program, which we call ROSE, an acronym for Relationship to One Selected Environment. We selected E_T ($i = 58$, ΔE of the electronic absorption maximum of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide),[4] which has been measured in 47 of our 61 solvents. Before applying ROSE, we calculated all 61 E_T values by a nonlinear least-squares procedure[63] using all 1080 data in Table II. Then we used these 61 calculated E_T values as A values and correlated all 77 reactions by eq 1. The section named Correlation Coefficients explains why it is acceptable and preferable to use calculated E_T values here instead of observed E_T values. This first procedure, using eq 1 with ROSE, gives $C_i = 0.986$ for E_T ($i = 58$) but only 0.808 for Y ($i = 12$), 0.713 for CH_3Br solvolysis ($i = 1$), and 0.780 for UV absorption of $4\text{-}Et_2NC_6H_4NO_2$ ($i = 50$). The overall C for all 77 reactions (with 928 degrees of freedom) is 0.873.

Second, to obtain the *best* possible fit consistent with eq 1, we used the 1080 data to optimize all of the constants in eq 1 by nonlinear least squares, not only all the reaction constants a_i and c_i but also the solvent constants A_j. We call this program LOVE, an acronym for Lone Optimal Vector Evaluation, referring to the single solvent vector **A**. Then $C_i = 0.971$ for E_T but only 0.929 for Y, 0.712 for CH_3Br solvolysis, and 0.868 for $4\text{-}Et_2NC_6H_4NO_2$. The overall C for all 77 reactions (with 867 degrees of freedom) is 0.890.

These correlations with eq 1 fail to meet our minimum standard of an overall C exceeding 0.965.

Solvent Effect Predictions Based on Two Constants per Solvent

Equation 2 involves two solvent vectors **A** and **B** in a dual linear

$$p_{ij} = a_iA_j + b_iB_j + c_i \tag{2}$$

(or "planar") free energy relationship for predicted solvent effects p_{ij}. This was used by us in 1955[64] and subsequently by Winstein and other investigators.[7] Recently,[63] a rational general method was developed for evaluating all the constants in eq 2, not only all the reaction constants a_i, b_i, and c_i but also the two vectors **A** and **B**. We call this method DOVE, an acronym for Dual Obligate Vector Evaluation. Two critical subsidiary conditions that are true and accurate must be identified and incorporated into the solution (in addition to the four arbitrary subsidiary conditions that determine references and scale factors) to force A and B values to represent physically significant influences that are cleanly separated, i.e., not hybrids or linear combinations of such influences. This method was applied to substituent effects in the previous paper[62] (using critical conditions that force B_j to represent the influence that the jth substituent exerts through resonance but A_j to represent all its nonresonance influences).

It is considerably more difficult to find acceptable critical conditions for the solvent effect problem than for the substituent effect problem. We believe that the most important solvent properties affecting chemical reactivity are *anion-solvating tendency* and *cation-solvating tendency*. We shall symbolize these solvent characteristics by A and B, respectively, and coin the names "acity" and "basity", because, although they are obviously kinds of acidity and basicity, they are neat (bulk) solvent properties involved in solvations, i.e., specific local electrostatic interactions with polar centers in the solutes that usually do not involve major covalency changes and so are usually omitted from chemical equations. Another difficulty arises because salts in solution generally have both their anions and their cations significantly solvated. One can evaluate mean ionic activity coefficients but not single-ion activity coefficients. A further complication that arises if one tries to associate critical conditions with reaction constants or ratios or differences of reaction constants is the fact that measured data reflect only a difference between transition state and reactants for kinetic data, between two transition states for product ratios, between products and reactants for equilibria, or between excited and ground states for spectra.

Our earlier two-vector analysis of solvent effects[64] incorporated as its two critical conditions the assumptions that a_i/b_i for methyl bromide solvolysis is only one-third of that for *tert*-butyl chloride solvolysis, whereas a_i/b_i for triphenylmethyl fluoride solvolysis is three times that for *tert*-butyl chloride. Few persons would deny that the trend in relative sensitivities is qualitatively in that direction. However, there was no quantitative justification for the ratios chosen (0.33 and 3), and it is an unfortunate fact that quantitative inaccuracy in any critical condition can introduce unexpected and erroneous inversions of orders in the constants produced. (In the light of the present study, it now appears that these ratios should have been −0.94 and +6.26).

Therefore it seems preferable to associate all subsidiary conditions with the solvents, none with the reactions. For the four arbitrary conditions, which set zeros and scale factors but do not affect rank orders, we now choose $A = B = 0$ for *n*-heptane and $A = B = 1$ for water. These need no justification because any references or units are equally acceptable and results are easily transformed from one such set to another. For the two critical conditions, we choose $A = 0$ for hexamethylphosphoric triamide ($((CH_3)_2N)_3PO$, HMPA) and $B = 0$ for trifluoroacetic acid (CF_3CO_2H, TFA). This is equivalent to the assumptions that *HMPA is practically as poor an anion solvator, and TFA is practically as poor a cation solvator, as n-heptane* or other saturated hydrocarbons. They should certainly not be quite as poor, but the differences must be exceedingly small; hence these should be good approximations. The positive end of HMPA has its charge delocalized over two nitrogens and is coated and insulated from solvent by six methyl groups, making it very hydrocarbon-like. The negative end of TFA is close to the CF_3 group because of the large inductive effect of CF_3 ($F = 0.64$[62]); this CF_3 group is hydrophobic, very poor at solvating ions, and so should effectively insulate the negative end of TFA from solvent. We choose these conditions ($A_{\text{HMPA}} = 0$ and $B_{\text{TFA}} = 0$) because no other high-B solvent out of our 61 has a lower A and no other high-A solvent out of our 61 has a lower B. No A or B value is then negative for any solvent. If anyone in the future discovers a solvent for which data in three or more reactions generate a negative A or B, one could then easily adopt $A = 0$ or $B = 0$ for it instead and retransform all the solvent and reaction constants accordingly. This change would force A to be slightly positive for HMPA or B to be slightly positive for TFA, but shifts in A and B values would be relatively minor.

One might expect solvent effects to be more complicated functions than that represented by eq 2. They might involve also $A_j \times B_j$ product terms or other powers than first. In fact they do not, because with eq 2 and all 1080 data in Table II, the overall C[61] (with 733 degrees of freedom) is 0.9906 and no individual reaction is less than 0.975. The overall determination or decision coefficient (square of 0.9906) is 0.9813. This 98% represents the fraction of these solvent effects that is "explained" or attributable to changes in A or B as predicted by eq 2 rather than due to random experimental error or other factors not accounted for by eq 2. The fits are so good that no other terms are needed or justifiable. The uncertainty[65] (standard deviation) of this determination coefficient is 0.0013; the uncertainty of the 0.9906 is 0.0007; these uncertainties are reliable to ±5% (within 0.0001).

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[61] See section on Correlation Coefficients for calculation of corrected correlation coefficients C and C_i.

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Table III. Solvent Constants, *A* and *B*, from DOVE Analysis of Data in Table II

j	Solvent molecular formula	condensed structure	Acity = A	std dvn +/-	Basity = B	st dv +/-	no. of i's	correl coeff C
1	CCL4	CCL4	0.09	.02	0.34	.02	35	.9869
2	CHCL3	CHCL3	0.42	.01	0.73	.02	22	.9897
3	CH2CL2	CH2CL2	0.33	.01	0.80	.03	26	.9822
4	CH2O2	HCOOH	1.18	.03	0.51	.03	12	.9948
5	CH3NO	HCONH2	0.66	.02	0.99	.03	8	.9700
6	CH3NO2	MeNO2	0.39	.02	0.92	.03	20	.9805
7	CH4O	MeOH	0.75	.01	0.50	.02	55	.9916
8	CS2	CS2	0.10	.02	0.38	.02	18	.9868
9	C2CL4	CL2CCCL2	0.10	.03	0.25	.03	6	.9883
10	C2HCL3	CLCHCCL2	0.16	.05	0.54	.03	3	.9713
11	C2HF3O2	CF3COOH	1.72	.05	0.00	.00	8	.9956
12	C2H3N	MeCN	0.37	.01	0.86	.02	44	.9894
13	C2H4CL2	CLCH2CH2CL	0.30	.02	0.82	.02	24	.9923
14	C2H4O2	MeCOOH	0.93	.03	0.13	.03	20	.9902
15	C2H6O	EtOH	0.66	.01	0.45	.02	52	.9923
16	C2H6OS	MeSOMe	0.34	.02	1.08	.04	29	.9930
17	C2H6O2	HOCH2CH2OH	0.78	.02	0.84	.03	14	.9882
18	C3H6O	MeCOMe	0.25	.01	0.81	.03	36	.9911
19	C3H7NO	HCONMe2	0.30	.01	0.93	.03	29	.9920
20	C3H8O	CH3CH2CH2OH	0.63	.02	0.44	.03	15	.9982
21	C3H8O	Me2CHOH	0.59	.02	0.44	.02	27	.9957
22	C4H8O	MeCOEt	0.23	.02	0.74	.03	9	.9874
23	C4H8O	(CH2)4O	0.17	.01	0.67	.02	26	.9913
24	C4H8O2	MeCOOEt	0.21	.02	0.59	.02	18	.9893
25	C4H8O2	O(CH2CH2)2O	0.19	.01	0.67	.02	25	.9898
26	C4H9NO	MeCONMe2	0.27	.02	0.97	.04	8	.9849
27	C4H1oO	BuOH	0.61	.02	0.43	.02	23	.9952
28	C4H1oO	EtOEt	0.12	.02	0.34	.02	28	.9963
29	C4H1oO	Me3COH	0.45	.01	0.50	.03	18	.9718
30	C4H1oO2	MeOC2H4OMe	0.21	.02	0.50	.11	16	.9963
31	C4H11N	BuNH2	0.15	.04	1.17	.06	4	.9987
32	C5H5N	(CH)5N	0.24	.02	0.96	.04	20	.9932
33	C6H5Br	PhBr	0.22	.02	0.66	.02	21	.9772
34	C6H5CL	PhCL	0.20	.02	0.65	.02	27	.9911
35	C6H5NO2	PhNO2	0.29	.02	0.86	.03	19	.9895
36	C6H6	PhH	0.15	.01	0.59	.02	45	.9932
37	C6H7N	PhNH2	0.36	.02	1.19	.05	9	.9901
38	C6H1oO	(CH2)5CO	0.25	.03	0.79	.04	4	.9900
39	C6H12	(CH2)6	0.02	.02	0.06	.01	34	.9938
40	C6H14	Me(CH2)4Me	0.11	.02	-0.01	.02	19	.9956
41	C6H15N	Et3N	0.08	.03	0.19	.04	11	.9923
42	C6H18N3OP	(Me2N)3PO	0.00	.00	1.07	.05	5	.9988
43	C7H5N	PhCN	0.30	.02	0.87	.03	11	.9949
44	C7H8	PhMe	0.13	.01	0.54	.02	29	.9920
45	C7H8O	PhOMe	0.21	.02	0.74	.03	8	.9913
46	C7H9N	PhNHMe	0.40	.03	1.07	.05	3	.9834
47	C7H9N	2,6-C5H3NMe2	0.18	.02	0.81	.08	4	.9789
48	C7H16	Me(CH2)5Me	0.00	.00	0.00	.00	11	.9981
49	C8H8O	PhCOMe	0.23	.02	0.90	.03	11	.9908
50	C8H1o	o-C6H4Me2	0.06	.04	0.53	.02	4	.9993
51	C8H1o	m-C6H4Me2	0.04	.05	0.54	.02	4	.9975
52	C8H1o	p-C6H4Me2	0.06	.03	0.50	.02	7	.9945
53	C8H18	Me3CCH2CHMe2	0.01	.02	-0.03	.08	6	.9839
54	C8H18O	Bu2O	0.06	.02	0.28	.03	8	.9916
55	H2O	H2O	1.00	.00	1.00	.00	28	.9914
56	H2O	96% MeOH	0.76	.02	0.61	.03	6	.9864
57	H2O	80% EtOH	0.75	.02	0.65	.02	19	.9977
58	H2O	60% EtOH	0.80	.02	0.77	.03	8	.9910
59	H2O	50% EtOH	0.82	.02	0.80	.03	8	.9865
60	H2O	80% MeCOMe	0.62	.02	0.70	.03	7	.9888
61	H2O	70% MeCOMe	0.66	.02	0.74	.03	6	.9758

One might also expect other specific solvent properties to be important in addition to anion-solvating tendency and cation-solvating tendency such as hydrogen-bonding acidity, hydrogen-bonding basicity, electrophilicity, and nucleophilicity. The high correlations show that they are not. Evidently there is a *remarkable parallelism among* three neat solvent properties, i.e., *anion-solvating tendency, hydrogen-bonding acidity, and electrophilicity*, since for these 1080 diverse data they can all be adequately represented by a single number for each solvent, its acity *A*. Likewise, three other neat solvent properties, *cation-solvating tendency, hydrogen-bonding basicity, and nucleophilicity*, are all adequately represented by another single number, its basity *B*.

One is even more surprised not to have to include a third solvent factor to represent "lipophilicity" or "hydrophobicity".[66] However, our C_i's are so high, even for distributions of organic compounds such as phenols and aldehydes between organic and aqueous layers (i = 35–41), that there seems to be no need for more solvent constants than just the *A* and *B* values.

1. Solvent Constants. Figure 1 is a computer-generated plot of *B* vs. *A* showing that these are highly variable but essentially independent solvent properties. The determination coefficient (square of the *C* between *A* and *B*) is −0.0162. The uncertainty[65] (standard deviation) of this determination coefficient is 0.0017 ± 0.0001. Hence, surprisingly, there is no correlation at all between *A* and *B*, in spite of our earlier expectation of a substantial negative correlation, because strong acids are usually weak bases and strong bases are usually weak acids.

Table III lists *A*, *B*, and their uncertainties[65] (standard deviations), number of reactions, and correlation coefficient C_j for each of the 61 solvents, ordered by molecular formula, following *Chemical Abstracts* Formula Index. Since our computer-controlled printer could neither subscript nor backspace and since zero vs. capital O and unity vs. letter l differences were inadequate, we substituted lower case letter o for zero, CL for Cl, Me for CH_3, Et for C_2H_5, Bu for C_4H_9, and Ph for C_6H_5. Tables IV and V include common and systematic names respectively for each *j*.

Solvents with high *B* and low *A* are best for enhancing the reactivity of anionic solutes.[67] Hexamethylphosphoramide (HMPA), dimethyl sulfoxide, dimethylacetamide, dimethylformamide, 1,2-dichloroethane, methylene chloride, nitro compounds, nitriles, and ketones are best for this purpose. Pyridine, aniline, and *n*-butylamine are also in this group but more often cause trouble by competing as nucleophiles. Other halides, ethers, esters, triethylamine, and aromatic hydrocarbons are poorer solvators of cations.

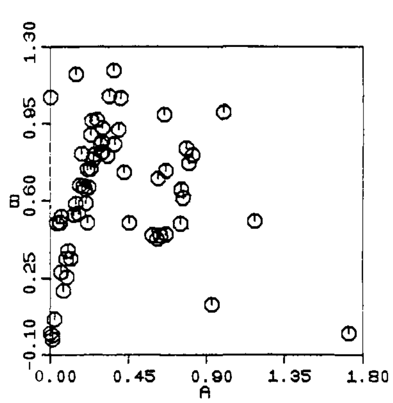

Figure 1. Computer-produced plot of solvent basity vs. solvent acity. The most NW, NE, SE, and SW points are $((CH_3)_2N)_3PO$, H_2O, CF_3CO_2H, and *n*-C_7H_{16}. Other peripheral points (*A*, *B*) are *n*-$C_4H_9NH_2$ (0.15, 1.17), $C_6H_5NH_2$ (0.36, 1.19), HCO_2H (1.18, 0.51), and CH_3CO_2H (0.93, 0.13).

Solvent *A* values decrease in the order CF_3CO_2H (1.8); HCO_2H (1.2); H_2O (1.0); CH_3CO_2H (0.95); $HOCH_2CH_2OH$ (0.78); MeOH (0.76); EtOH (0.67); *i*-PrOH (0.60); *t*-BuOH (0.45); $CHCl_3$ (0.41); C_6H_6 (0.12); CCl_4 (0.08). *B* values of CF_3CO_2H (0.00) and CH_3CO_2H (0.15) are very low. A high *A* and low *B* can be useful (1) to avoid nucleophilic involvement of the solvent in unwanted covalent-bond formation between solvent and solute or (2) to enhance reactivity of solute cations. Compared to CH_3CO_2H (A = 0.95, B = 0.15), EtOH has a much lower *A* and much higher *B* (A = 0.67, B = 0.45) and *t*-BuOH has a still lower *A* and higher *B* (A = 0.45, B = 0.50).

Table IV lists the solvents in order of their sum $A + B$, which can reasonably be called "polarity". Here H_2O (2.0), HCO_2H (1.73), $HOCH_2CH_2OH$ (1.62), and CH_3OH (1.38) are high on the list because both *A* and *B* are high. Heptane is at the bottom. Polarity is the distance in a northeasterly direction from a $B = -A$ line on Figure 1. Data for reactions having *a* and *b* approximately equal are good linear functions of this sum alone. They include the *Y* from solvolysis of *tert*-butyl chloride (i = 12), log *k* for bromination of 1-pentene (i = 30), ΔG for distribution of $Et_4N^+I^-$ between solvents (i = 42), and UV absorption energies of a merocyanine dye (Brooker's χ_R, i = 60). However, *Z* (i = 43), E_T (i = 58), and Ω (i = 33) represent reactions that are more sensitive to *A* than to *B*, and many other reactions differ even more between *a* and *b*.

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[66] Ben-Naim, A. "Hydrophobic Interactions"; Plenum Press: New York, 1980. Tanford, C. "The Hydrophobic Effect", 2nd ed.; Wiley: New York, 1980.

[67] Reference 3b, pp 334–342. Reference 6, pp 51, 148–155, 159–161.

Table IV. Solvent Constants in Order of Decreasing Solvent Polarity, $A + B$

j	Solvent common name	Polar-ity =A+8	st dv +/-	j	Solvent common name	Polar-ity =A+8	st dv +/-	j	Solvent common name	Polar-ity =A+B	st dv +/-
55	water	2.00	.00	43	benzonitrile	1.16	.03	23	tetrahydrofuran	0.84	.03
11	trifluofoacetic acid	1.72	.05	2	chloroform	1.15	.03	24	ethyl acetate	0.79	.03
4	formic acid	1.69	.03	35	nitrobenzene	1.14	.03	36	benzene	0.73	.02
5	formamide	1.65	.03	3	methylene chloride	1.13	.03	30	monoglyme	0.72	.10
59	50% ethyl alcohol	1.63	.03	49	acetophenone	1.13	.03	10	trichloroethylene	0.70	.04
17	ethylene glycol	1.62	.03	13	ethylene chloride	1.12	.03	44	toluene	0.67	.02
58	60% ethyl alcohol	1.57	.02	15	ethyl alcohol	1.11	.02	50	o-xylene	0.59	.04
37	aniline	1.56	.05	20	n-propyl alcohol	1.08	.03	52	p-xylene	0.56	.03
46	N-methylaniline	1.47	.04	42	hexametapol	1.07	.05	51	m-xylene	0.54	.05
16	dimethyl sulfoxide	1.41	.04	14	acetic acid	1.06	.04	8	carbon disulfide	0.48	.02
57	80% ethyl alcohol	1.40	.02	18	acetone	1.06	.03	28	diethyl ether	0.46	.02
61	70% acetone	1.40	.02	27	n-butyl alcohol	1.04	.02	1	carbon tetrachloride	0.43	.02
56	96% methyl alcohol	1.38	.02	38	cyclohexanone	1.04	.04	9	perchloroethylene	0.35	.03
60	80% acetone	1.32	.03	21	isopropyl alcohol	1.03	.02	54	di-n-butyl ether	0.34	.03
31	n-butylamine	1.32	.05	47	2,6-lutidine	0.99	.08	41	triethylamine	0.27	.04
6	nitromethane	1.31	.03	22	methyl ethyl ketone	0.97	.03	39	cyclohexane	0.09	.02
7	methyl alcohol	1.25	.02	45	anisole	0.96	.03	40	n-hexane	0.00	.03
26	dimethylacetamide	1.23	.04	29	t-butyl alcohol	0.95	.03	48	n-heptane	0.00	.00
19	dimethylformamide	1.23	.03	33	bromobenzene	0.88	.03	53	isooctane	0.01	.08
12	acetonitrile	1.22	.03	25	dioxane	0.86	.03				
32	pyridine	1.20	.04	34	chlorobenzene	0.85	.03				

Table V. Solvent Constants in Order of the Difference $B - A$

j	Solvent Chem. Abstr. or IUPAC name	8-A	st dv +/-	j	Solvent Chem. Abstr. or IUPAC name	8-A	st dv +/-	j	Solvent Chem. Abstr. or IUPAC name	8-A	st dv +/-
42	phosphoric triamide, Me6-	1.07	.05	25	1,4-dioxane	0.48	.02	17	1,2-ethanediol	0.06	.04
31	1-butanamine	1.03	.08	50	benzene, 1,2-dimethyl-	0.46	.05	29	2-propanol, 2-methyl-	0.05	.03
37	benzenamine	0.83	.06	51	benzene, 1,3-dimethyl-	0.46	.05	39	cyclohexane	0.04	.02
16	methane, sulfinylbis-	0.74	.04	34	benzene, chloro-	0.45	.03	48	heptane	0.00	.00
32	pyridine	0.72	.04	52	benzene, 1,4-dimethyl-	0.44	.04	55	dihydrogen oxide	0.00	.00
26	ethanamide, N,N-dimethyl-	0.70	.04	33	benzene, bromo-	0.44	.03	59	50% ethanol (by vol.)	-0.02	.04
49	ethanone, 1-phenyl-	0.67	.04	36	benzene	0.44	.02	40	hexane	-0.02	.02
46	benzenemethanamine	0.66	.07	44	benzene, methyl-	0.40	.02	58	60% ethanol (by vol.)	-0.03	.05
47	pyridine, 2,6-dimethyl-	0.63	.09	24	ethanoic acid ethyl ester	0.38	.03	53	pentane, 2,2,4-trimethyl-	-0.04	.08
19	methanamide,N,N-dimethyl-	0.63	.04	10	ethene, trichloro-	0.38	.06	57	80% ethanol (by vol.)	-0.10	.03
43	benzonitrile	0.57	.04	5	methanamide	0.33	.05	21	2-propanol	-0.14	.03
35	benzene, nitro-	0.57	.03	2	methane, trichloro-	0.31	.03	56	96% methanol (by vol.)	-0.15	.04
18	2-propanone	0.55	.03	30	ethane, 1,2-dimethoxy-	0.29	.12	27	1-butanol	-0.19	.03
38	cyclohexanone	0.54	.05	8	methane, dithio-	0.27	.02	20	1-propanol	-0.19	.03
45	benzene, methoxy-	0.53	.04	1	methane, tetrachloro-	0.25	.02	15	ethanol	-0.21	.02
6	methane, nitro-	0.53	.04	28	ethane, 1,1'-oxybis-	0.22	.03	7	methanol	-0.25	.03
13	ethane, 1,2-dichloro-	0.52	.03	54	butane, 1,1'-oxybis-	0.22	.05	4	methanoic acid	-0.67	.05
22	2-butanone	0.51	.04	9	ethene, tetrachloro-	0.16	.06	14	ethanoic acid	-0.81	.05
23	furan, tetrahydo-	0.50	.03	41	ethanamine, N,N-diethyl-	0.12	.05	11	ethanoic acid,trifluoro-	-1.72	.05
12	ethanenitrile	0.49	.03	60	80% 2-propanone (by vol.)	0.08	.04				
3	methane, dichloro-	0.48	.03	61	70% 2-propanone (by vol.)	0.07	.04				

Table V lists the solvents in order of the difference $B - A$, ranging from n-$BuNH_2$ to CF_3CO_2H. $B - A$ is the distance in a northwesterly direction from a $B = A$ line on Figure 1. On this scale, saturated hydrocarbons, H_2O, $HOCH_2CH_2OH$, and t-BuOH occupy a middle or neutral position. However, with amides, haloalkanes, and benzene, B predominates significantly, whereas A overbalances it slightly ($B - A$ is negative) for i-PrOH, EtOH, and MeOH. Obviously we could now just as well express the 1080 data as functions of polarity ($A + B$) and this difference ($B - A$) and obtain the same correlation coefficients, because $A + B$ and $B - A$ are just as independent and uncorrelated with one another as are A and B. However, we shall stick with A and B because they seem to us to be more directly and simply related to the physical solvent–solute interactions that affect chemical reactivity.

Solvent properties not well correlated by A and B are melting point, boiling point, refractive index, dielectric constant, dipole moment, autoprotolysis constant, and maximum acceptable concentration in workroom air. These are conveniently tabulated in Reichardt's book.[68] These, and prices, often constitute practical considerations that affect a choice between solvents of suitable chemical reactivity.

Schleyer assumed that formic acid and acetic acid have equal B values as one of the critical subsidiary conditions in his dual-vector analyses of solvent effects.[69] However, this is contradicted by our constants for formic acid ($j = 4$, $A = 1.18$, $B = 0.51$) and acetic acid ($j = 14$, $A = 0.93$, $B = 0.13$). *Formic acid is a considerably better cation solvator than acetic acid*, as well as being a better anion solvator. In fact, the difference in B values (0.38) is even larger than the difference in A values (0.25). Failure of this critical subsidiary condition to be true invalidates any simple physical interpretation of Schleyer's solvent parameters or reaction parameters. The incorrect condition was adopted because formic and acetic acids have similar rates of reaction with $(CH_2)_4Cl^+$ in SO_2 at −66 °C.[70] However, there are at least three weaknesses to that justification: (1) the acids were solutes, not neat (bulk) solvents; (2) the temperature was −66 °C, not 25 °C; (3) reactions of cations are relatively insensitive to differences between nucleophiles because higher nucleophilicity is usually largely offset by stabilization of the cationic reactant by the higher cation-solvating tendency associated with a better nucleophile; i.e., one is using a small difference between two large effects working in opposite directions and almost compensating each other.[71]

2. Reaction Constants. In Figure 2, a–h are computer-generated plots of observed vs. predicted data for a typical 8 of the 77 reaction series. Points are shown for all solvents, but arrows and labeling j numbers are omitted by the computer where they would otherwise overlap, with labeling preference being given to methanol ($j = 7$), acetic acid ($j = 14$), ethanol ($j = 15$), and water ($j = 55$). See Software for more on how these plots were produced. The distribution of solvents along the lines varies widely because it depends on a/b, but all of the fits are good. They are typical in that their average C_i is 0.9906, the same as the overall C for all 77, and the number of points nj_i per plot averages 16, close to the average of 14 for all 77.

Table VI is a computer-generated table that lists a, b, c, their uncertainties,[65] number of solvents, and C_i for each of the 77 reactions.

A simple reaction that comes close to measuring A in pure form is UV absorption by $(C_6H_5)_2C{=}O$ ($n \rightarrow \pi^*$, $i = 51$, $a = 1.87$, $b = -0.05$). Evidently its ground state can be stabilized by interaction of an oxygen lone pair with an A site in the solvent, but interaction of its carbonyl carbon with any B site is relatively negligible.

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(68) Reference 6, pp 33, 263–286, 318–321.

(69) Bentley, T. W.; Schadt, F. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 992; **1976**, *98*, 7667. Reference 6, pp 234–5.

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

(71) Another example of such insensitivity is solvolysis of *tert*-butyldimethylsulfonium ion (Swain, C. G.; Kaiser, L. E.; Knee, T. E. C. *J. Am. Chem. Soc.* **1958**, *80*, 4093) where relative rates for H_2O, CH_3CO_2H, EtOH, and 90% acetone–10% water are 1.00, 1.28, 2.55, and 3.24 (range of log k is only 0.51).

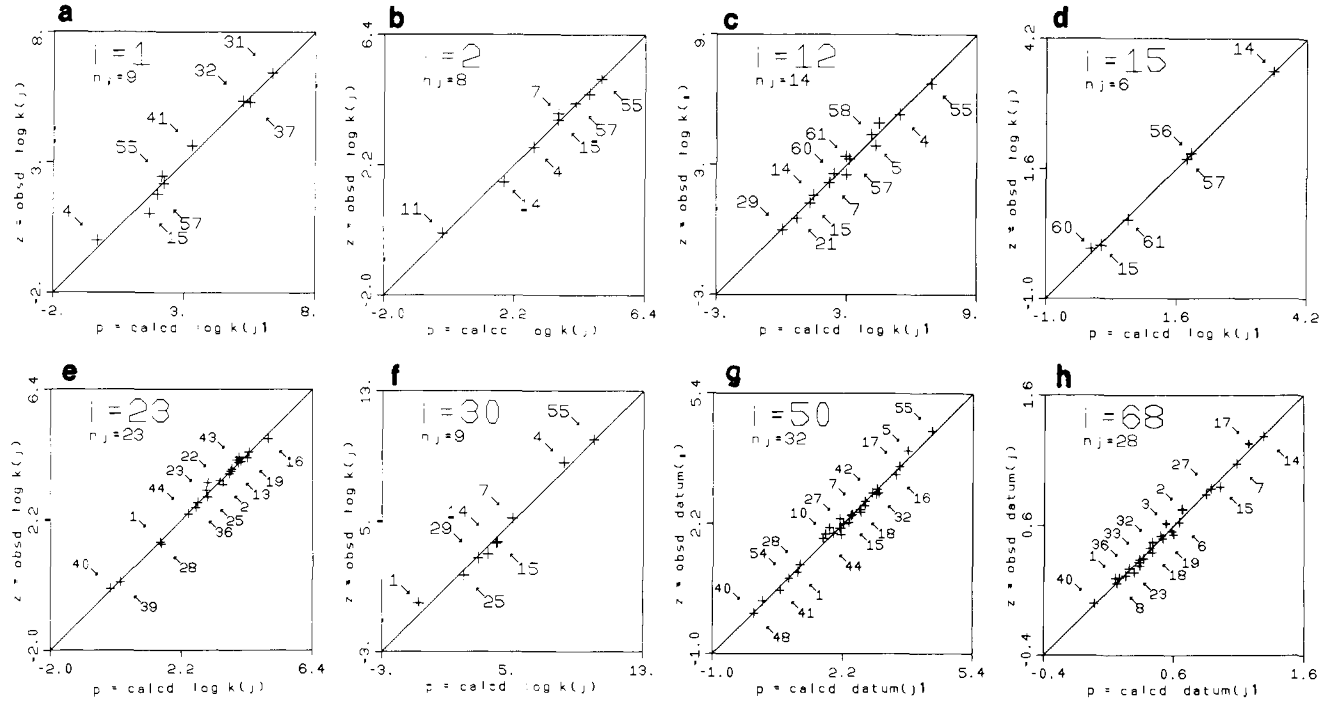

Figure 2. Computer-produced plots of observed vs. calculated data for a typical 8 of the 77 reactions *i*. The number of points is *nj*. Each arrow is labeled with the solvent *j*. See Table I for reactions *i*, Table III for solvents *j*.

Table VI. Reaction Constants, *a* and *b*, from DOVE Analysis of Data in Table II

Reaction i	A-sensitivity&stdv a	+/-	B-sensitivity&stdv b	+/-	c = p for j=48	st dv +/-	no. of j's	correl coeff C
1	-4.23	0.41	3.44	0.46	2.95	0.46	9	.9831
2	-1.91	0.27	3.71	0.29	3.20	0.39	8	.9935
3	-1.19	0.26	3.84	0.30	-0.49	0.27	11	.9906
4	-0.56	0.34	4.40	0.28	-0.82	0.30	9	.9939
5	3.46	0.22	3.75	0.25	-3.49	0.29	9	.9906
6	4.61	0.21	4.03	0.21	-4.75	0.23	7	.9979
7	5.49	0.22	4.36	0.23	-5.69	0.25	7	.9989
8	5.69	0.29	3.74	0.31	-5.29	0.35	7	.9959
9	6.69	0.35	4.62	0.37	-6.33	0.40	7	.9957
10	13.00	0.93	8.99	0.79	-11.74	0.98	9	.9934
11	7.85	0.50	4.45	0.59	-8.13	0.65	7	.9934
12	7.37	0.54	5.64	0.49	-6.10	0.46	14	.9852
13	5.63	0.41	6.13	0.44	-6.16	0.44	8	.9946
14	4.74	0.37	1.38	0.35	-2.18	0.38	8	.9950
15	14.88	1.10	1.82	0.63	-10.58	0.98	6	.9984
16	10.28	1.02	1.06	0.60	-6.93	0.99	6	.9880
17	0.56	0.21	4.61	0.23	-0.38	0.11	33	.9919
18	1.00	0.17	4.58	0.21	-0.29	0.09	14	.9972
19	1.56	0.24	4.95	0.26	-0.30	0.14	14	.9930
20	1.49	0.20	4.95	0.25	-0.27	0.13	14	.9946
21	0.91	0.16	4.52	0.20	-0.27	0.09	14	.9980
22	0.75	0.16	4.40	0.19	-0.30	0.10	14	.9971
23	0.94	0.61	4.38	0.29	-0.04	0.09	23	.9938
24	3.66	0.38	2.40	0.20	-0.42	0.12	15	.9922
25	3.18	0.30	2.34	0.17	-0.30	0.09	15	.9958
26	9.67	0.59	-0.04	0.77	0.00	0.82	10	.9963
27	3.05	0.38	-3.11	0.49	1.82	0.44	6	.9957
28	-1.86	1.35	4.74	0.62	-0.04	0.18	9	.9836
29	3.01	2.10	4.84	0.90	-0.38	0.12	5	.9993
30	7.21	0.56	6.34	0.82	-3.57	0.52	9	.9867
31	7.12	0.48	6.27	0.56	-2.71	0.43	7	.9901
32	3.27	0.22	1.03	0.18	-0.18	0.15	9	.9853
33	0.47	0.03	0.12	0.03	-0.07	0.03	11	.9747
34	1.27	0.07	0.35	0.08	-0.24	0.06	6	.9946
35	-0.77	1.52	2.40	0.51	0.11	0.07	7	.9898
36	-0.85	0.21	1.80	0.10	0.00	0.02	9	.9989
37	-3.18	0.76	4.49	0.36	-0.04	0.11	12	.9856
38	0.52	0.33	1.95	0.17	0.07	0.05	12	.9931
39	0.41	0.31	1.57	0.17	-0.57	0.06	8	.9939
40	0.10	0.32	2.38	0.16	-0.01	0.03	9	.9981
41	0.97	0.31	2.03	0.16	-0.03	0.04	9	.9971
42	11.44	0.67	9.13	0.74	-4.23	0.56	21	.9841
43	45.35	2.12	8.40	2.11	-12.52	1.99	22	.9855
44	44.29	2.20	7.91	1.93	-12.94	1.99	14	.9909
45	8.21	0.42	0.19	0.44	0.37	0.27	16	.9849
46	11.85	0.68	-1.88	0.58	0.51	0.37	16	.9832
47	10.92	0.69	-2.09	0.65	-0.25	0.34	7	.9932
48	0.58	0.18	1.78	0.20	0.00	0.05	6	.9962
49	0.59	0.10	2.21	0.10	0.02	0.04	26	.9957
50	1.66	0.12	2.72	0.13	0.02	0.06	32	.9938
51	1.87	0.07	-0.05	0.06	-0.02	0.04	11	.9967
52	2.08	0.07	-0.13	0.07	0.01	0.04	20	.9927
53	3.57	0.10	0.11	0.09	-0.00	0.06	22	.9962
54	3.37	0.23	0.29	0.25	-0.22	0.13	7	.9938
55	3.24	0.13	0.29	0.15	-1.03	0.15	13	.9908
56	22.69	1.37	1.92	1.44	-7.60	1.52	8	.9883
57	3.20	0.11	-0.35	0.13	-0.04	0.10	27	.9901
58	30.36	1.02	4.45	1.12	-1.78	0.80	47	.9839
59	26.71	1.10	2.29	1.15	-4.65	0.96	20	.9872
60	6.64	0.46	6.01	0.42	-0.11	0.25	34	.9855
61	10.16	0.60	-1.39	0.58	-0.07	0.44	22	.9776
62	5.77	0.34	-1.49	0.32	0.18	0.25	17	.9845
63	2.90	4.99	-0.86	1.09	0.08	0.09	7	.9996
64	29.52	1.97	11.35	1.63	1.12	0.95	19	.9845
65	11.69	5.42	13.94	2.64	-0.06	0.67	9	.9846
66	1.86	6.28	13.66	2.40	-0.36	0.45	11	.9891
67	41.01	6.52	11.08	3.02	0.50	1.06	13	.9854
68	1.40	0.05	0.13	0.05	-0.03	0.04	28	.9912
69	1.24	0.05	0.13	0.04	0.00	0.03	27	.9915
70	1.35	0.04	0.17	0.05	-0.01	0.03	28	.9913
71	1.57	0.08	0.37	0.09	-0.29	0.07	10	.9921
72	1.60	0.05	0.22	0.06	-0.25	0.05	10	.9979
73	1.53	0.05	0.21	0.06	-0.24	0.04	10	.9976
74	1.70	0.08	0.30	0.11	-0.28	0.08	10	.9920
75	4.00	0.16	0.06	0.21	-0.54	0.16	10	.9935
76	6.22	0.21	-0.61	0.21	-0.01	0.15	28	.9931
77	59.68	1.90	-1.55	2.07	-0.46	1.68	26	.9959

No reaction comes very close to measuring *B* in pure form. Gutmann's donor number DN[72] might be expected to approximate *B*, but in fact is not included in our 77 because it is not even a solvent effect. It was based on heats of coordination of $SbCl_5$ with the various "solvents" as solutes in 1% solutions in a common solvent, 1,2-dichloroethane, at 25 °C. This attempt to measure *B* directly has at least four fatal shortcomings: (1) the solvents are no longer neat but dilute solutions in $ClCH_2CH_2Cl$, unlike the other reactions; (2) because $ClCH_2CH_2Cl$ is a moderately strong cation solvator ($B = 0.81$) and in large excess, all differences are washed out between it and the 42 of our 61 solvents that are weaker cation solvators; (3) these are enthalpy, not free energy, differences, and linear relationships between ΔH and ΔG or ΔS have rarely if ever been demonstrated experimentally;[73] (4) $SbCl_5$, owing to the large-radius 5p orbitals and low electronegativity of Sb, is a poor model for the smaller alkali, ammonium, or carbon cationic or dipolar centers in the other reactions. For example, triethylamine has the highest DN of all, yet its *B* is only 0.19, less than diethyl ether or benzene, because in more typical organic reactions it suffers heavily from steric hindrance, which certainly affects free energies.

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[72] Reference 6, pp 16–18, 230–231.

[73] Petersen, R. C.; Markgraf, J. H.; Ross, S. D. *J. Am. Chem. Soc.* **1961**, *83*, 3819. Petersen, R. C. *J. Org. Chem.* **1964**, *29*, 3133.

Some reactions have a negative value for one of their reaction constants. This is a consequence of complexing interactions between anion- and cation-solvating centers in the solvent. Although these interactions are always the same in a given solvent, their effect on a reaction depends on the reaction in a qualitatively predictable way. Consider first the reaction of 4-nitrofluorobenzene with azide ion ($i = 26$, $a = 9.7$, $b = 0$). Fluorine is more sensitive to A solvation than other halides. This effect is not appreciably offset by complexing of azide ion with A centers in the solvent. Azide ion is a strong nucleophile but only a weak base and so is not seriously inhibited by increased complexing when higher A solvents are used. Next consider a typical Menschutkin reaction ($i = 23$, $EtI + Et_3N$, $a = 0.9$, $b = 4.4$). The decrease of a almost to zero is due to the lesser sensitivity of iodine to A solvation and to the lower nucleophilicity but higher basicity of the amine, causing more significant but undesirable complexing with higher A solvents. Finally consider methyl bromide solvolysis ($i = 1$, $a = -4.2$, $b = 3.4$). In spite of certainly higher sensitivity of Br than of I to anion solvation, higher A solvents now actually *retard* solvolysis. The nucleophile is now a hydroxylic solvent molecule, which must shed some of this A complexing to operate as a nucleophile or be less effective if it is still encumbered by such complexing at the transition state. Furthermore, the transition state should be later than in the preceding reactions, just because the nucleophile is poorer.[74] Consequently this adverse effect of higher A solvents is magnified and now is large enough to more than offset any help from better A solvation of Br. An opposite situation appears in the reaction of benzenesulfonyl chloride with aniline ($i = 27$, $a = 3.1$, $b = -3.1$), where the negative b suggests that higher B solvents seriously inhibit or interfere with effective A solvation of a sulfonyl oxygen needed to promote addition of the amine to the sulfur.

An oddity of our previous analysis of solvent effects[64] that surprised us and others[75] unexpectedly still persists in our present analysis. The sensitivity (b) to cation-solvating tendency of the solvent (B) actually *rises* from methyl bromide (3.44) to isopropyl tosylate (3.75) to 2-adamantyl tosylate (4.45) to *tert*-butyl chloride (5.64) to benzhydryl chloride (8.99) solvolysis. However, the sensitivity (a) of these solvolyses to the anion-solvating tendency of the solvent (A) rises even faster in general (from −4.23 to +13.00), thereby obscuring the fact that B solvation is involved. Nevertheless, B solvation is certainly heavily involved in hydrolyses and alcoholyses of all these halides and tosylates because these b values are all enormous compared to their uncertainties. Since secondary and tertiary halides and esters are even more sensitive ($b = 4.4$–9.0) to solvent B than methyl bromide ($b = 3.4$), at the transition state there must be stronger bonding between the solvent and the center in RX most susceptible to B attack. However, since the single solvent property B adequately represents both nucleophilicity and cation-solvating tendency for all the 88 diverse reactions, *solvent effects afford no operational distinction between nucleophilic assistance (covalent bonding) and cation solvation (ionic bonding) by the solvent.* Therefore at the transition state, solvent "nucleophilic assistance" and "cation solvation" are synonymous and one can and should use these terms interchangeably. This should dispel the long-standing myth that solvent nucleophilicity does not affect the rates of *tert*-butyl chloride and 2-adamantyl tosylate solvolyses.[76]

In the solvolysis of triphenylmethyl fluoride, b is at last much lower (1.82), but it is probably still not zero, since it is nearly three standard deviations above zero. It would be possible for b to be zero for the triphenylcarbonium ion in an equilibrium process and yet not be zero in this kinetic process because the carbonium ion has somewhat different geometry, solvation, and free energy than the transition state leading to it.

Table VII. Other Observed Solvent Effects, 75 Data for 11 Other Reactions, Used as Input for Linear Correlations of Table VIII[a]

```
78 4 4.54 14  0 57 2.331 58 3.48 59 4 08 \ 79 6 3 379 7 4.504 12 3 079 14 4 528
15 4.096 16 3.562 18 2 233 19 3.002 23 1.227 24 1.353 28  0 32 2 63 57 4 795
\ 80 7 2.457 15 2 308 18 2 529 24 2.093 28 .624 33 2 176 34 2 108 36 1 5'1 40  0
45 2.35 48  116 49 2.857 \ 81 7 2.101 14 .0 15 1 808 57 2 382 59 2 756 \ 82 4
3 092 11 4.248 14  0 57 .961 59 2.163 \ 83 4 3.109 14  0 57 .872 58 1 692 59 2 1
\ 84 4 3.038 14 .0 57 1 287 58 2.107 59 2 509 \ 85 4 6 477 11 8 049 14 4 301 15
3 718 16 3.179 18 1.602 23 .699 28 .0 \ 86 7  681 14 .296 15  0 57 1.42 59 2 533
\ 87 7 .556 14 .046 15 .0 57 1.019 59 1.714 \ 88 7 2.812 14 2 843 15 1 774 21
 907 29 .0 57 3 736 60 2.794
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[a] See footnote a of Table II. See text for reaction and reference for each i.

One of the anonymous referees suggested that we should explore other choices of critical conditions to see if we cannot find some that agree better with generally preconceived notions that b should decrease from isopropyl to *tert*-butyl to benzhydryl solvolyses and that B for formic acid should not exceed that for acetic acid. This referee was troubled that "TFA and HMPA, because of the presence of local dipoles, may not at all resemble n-heptane in the specified ion-solvating properties, as assumed in selecting the subsidiary conditions". Therefore we have added this paragraph to mention that we have tried 187 other sets of subsidiary conditions. One of the 188 sets allows us to increase the assumed B of TFA or the assumed A of HMPA above zero. Even with independent choices of 0, 0.1, and 0.3 for these constants (nine separate transformations), b always increases from isopropyl tosylate to *tert*-butyl chloride to benzhydryl chloride solvolyses, B for formic acid is always more than twice that for acetic acid, and most rank orders do not change. Furthermore, with $B_{TFA} = A_{HMPA} = 0.3$, for example, many of the other constants become chemically unreasonable: n-$BuNH_2$ has a lower B than water and HCO_2H has a lower A than water and A for acetic acid (at 0.71) is practically as low as A for methanol (0.68). Similar conflicts when we used others of our 188 sets of subsidiary conditions provided further evidence convincing us that B_{TFA} and A_{HMPA} must indeed be very close to zero.

The reaction most sensitive to solvent change is Kosower's Z (ΔE of UV absorption maximum of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide, $i = 43$, $a = 45.35$, $b = 8.40$). Dimroth's E_T is slightly less sensitive ($i = 58$, $a = 30.36$, $b = 4.45$). Although $i = 77$ has a numerically higher a, one should recognize that a and b values depend on the units chosen, and in comparable energy units no NMR, ESR, or IR series can compete with the most sensitive electronic spectra.

In any reaction, data for solvents that protonate, deprotonate, or otherwise covalently change a reactant must be excluded (see third reason under Scope). No carboxylic acid was included by Dimroth in his E_T series[4,48] because it would protonate the amine oxide indicator. Likewise, no carboxylic acids are included in other amine oxide or amine series (i = 17–25, 27, 45–47, 50, 52–56, 60, 64, 69, 71–76) where major protonation would occur, although measurements for a carboxylic acid solvent were made and reported in the literature for a few of these reactions. Sulfonic acids were improperly included in the AN series but not listed by Reichardt[6] nor used by us. They could not properly be added to any of our 77 reactions save possibly the solvolyses (i = 1–13) by further experimental work because they would protonate a basic atom in a reactant and so produce a sudden drastic change in the reaction from that occurring in the other solvents.

Temperature differences between reactions might be expected to hurt the correlations because A and B might change and change in different ways with temperature. Therefore we excluded reactions done below 20 °C and most done at 75 °C or above. Most of the 77 are at 25 ± 5 °C. However, reactions 1, 2, 4, and 14 were at 50 °C, and reaction 3 was at 75 °C. The similarly good correlations (0.991–0.993) for $i = 17$ at 20 °C ($CH_3I + Pr_3N$), $i = 2$ at 50 °C (CH_3OTs + solvent), and $i = 3$ at 75 °C (n-BuBr + solvent) suggest that the A and B values may be sufficiently constant and valid from 20 °C to 75 °C.

3. Extension to Other Reactions or Solvents can easily be accomplished by ordinary multiple linear least-squares regression by using A and B values for solvents from Table III as known independent variables to determine a, b, and c for new reactions or by using a, b, and c values for reactions from Table VI as known

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[74] Swain, C. G.; Thornton, E. R. *J. Am. Chem. Soc.* **1962**, *84*, 817. Thornton, E. R. *Ibid.* **1967**, *89*, 2915. Winey, D. A.; Thornton, E. R. *Ibid.* **1975**, *97*, 3102. Schowen, R. L. *Prog. Phys. Org. Chem.* **1972**, *9*, 275–332.

[75] Reference 6, p 235.

[76] Winstein, S.; Grunwald, E.; Jones, W. H. *J. Am. Chem. Soc.* **1951**, *73*, 2700, 2701, 2705. Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7658; *Adv. Phys. Org. Chem.* **1977**, *14*, 1–67.

Table VIII. Other Reactions Fitted with Predetermined *A* and *B* Constants

i	reactant	*a*	*b*	C_i
78	1-AdBr	7.56	7.16	0.9987
79	4-$MeOPhCMe_2CH_2OTs$	6.32	2.88	0.9966
80	EtI + Et_3N	1.63	2.73	0.9783
81	EtOTs	−2.65	3.64	0.9847
82	$Me_3CCHMeOBs$	6.16	4.20	0.9990
83	$PhCMe_2CH_2Cl$	6.53	4.10	0.9975
84	$PhCMe_2CH_2Br$	5.54	4.54	0.9978
85	$PhCMe_2CH_2OTs$	5.72	2.42	0.9940
86	*trans*-2-$BrC_6H_{10}OBs$	6.36	4.36	0.9994
87	*trans*-2-$MeOC_6H_{10}OBs$	3.79	3.12	0.9976
88	1-AdOTs	10.02	5.35	0.9975

independent variables to determine *A* and *B* for new solvents. It is not necessary to use DOVE or any nonlinear least-squares program but only to solve the three linear equations in three unknowns or two equations in two unknowns.[77]

Tables VII and VIII list 75 other data and 11 other reactions fitted later in this way by using *A* and *B* values already determined. The excellent fit of 1-adamantyl bromide solvolysis at 25 °C[78] ($i = 78$, $C = 0.999$) with $a = 7.56$ and $b = 7.16$ might seem surprising because this indicates major cation solvation, contrary to Schleyer's premise that none is involved because backside attack is impossible in this molecule. Our interpretation is that *front-side cation solvation is evidently practicable for a reaction forming a carbonium ion or ion pair.* Reaction 79 is Winstein's solvolysis of 4-$MeOPhC(Me)_2CH_2OTs$ at 75 °C,[79] which runs even in aprotic solvents and fits well ($C = 0.997$), strengthening our hypothesis that reactions at 75 °C may not require different *A* and *B* values. Even reaction 80 fits tolerably, in spite of being done at 100 °C (Et_3N + EtI, like $i = 23$ but at a 75 °C higher temperature). It is also of historical interest because this was the first study of solvent effects on a rate constant (by Professor Menschutkin at St. Petersburg University in 1890).[80] It is one of the tertiary amine quaternization reactions that are appropriately named after him.

Good correlations (*C* from 0.985 to 0.999) are also found for the next eight solvolyses ($i = 81$–88) as expected because their mechanisms should be similar to those of reactions already fitted. They include ethyl tosylate[81] (*p*-toluenesulfonate) at 50 °C, pinacolyl brosylate[82] (*p*-bromobenzenesulfonate) at 25 °C, neophyl chloride[83] and bromide[84] at 50 °C, and tosylate[85] at 75 °C, *trans*-2-bromocyclohexyl[81] and *trans*-2-methoxycyclohexyl[81] brosylate at 50 °C, and 1-adamantyl tosylate[86] at 25 °C. Ethyl tosylate undergoes direct solvent attack. The next six compounds involve various kinds of neighboring-group participation. The last one ionizes to a carbonium ion or carbonium tosylate ion pair intermediate in the rate-determining step. Nevertheless many reactions have solvent effects not fitted well by eq 2 ($C < 0.965$). Examples of and reasons for these misfits are considered in the next section.

Table IX. Relative *A* and *B* Sensitivities of 15 Alkyl Halides and Esters

i	reactant	*b*	*a*/*b*
16	Ph_3COAc	1.06	9.70
15	Ph_3CF	1.82	8.18
79	$PhMe_2CCH_2OTs$	2.42	2.36
88	1-AdOTs	5.35	1.87
11	2-AdOTs	4.45	1.76
83	$PhMe_2CCH_2Cl$	4.10	1.59
86	2-$BrC_6H_{12}OTs$	4.36	1.46
10	Ph_2CHCl	8.99	1.45
12	Me_3CCl	5.64	1.31
84	$PhMe_2CCH_2Br$	4.54	1.22
78	1-AdBr	7.16	1.06
13	Me_3CBr	6.13	0.91
5	Me_2CHOTs	3.75	0.92
81	EtOTs	3.64	−0.51
1	MeBr	3.44	−1.23

Winstein[76] considered *tert*-butyl chloride ($i = 12$) to be in a "limiting" category with no nucleophilic or partially covalent bonding of solvent to carbon at the transition state because of the similar solvent sensitivities of *trans*-2-bromocyclohexyl brosylate ($i = 86$). However, the *a*/*b* ratios listed in Table IX are certainly not limiting for those compounds (1.31–1.46) but are greatly exceeded by 2- and 1-adamantyl tosylates (1.76–1.87), neophyl tosylate (2.36), trityl fluoride (8.18), and trityl acetate (9.70). Claims for limiting behavior for *tert*-butyl chloride or adamantyl tosylates[76] are not really supported if one looks at all the relevant data.

Other solvents such as tetramethylurea, tetrahydrothiophene 1,1-dioxide (sulfolane), diphenyl ether, 2-methoxyethanol, and acetic anhydride have been measured in fewer than three of these reactions. It would be too risky to use *A* and *B* values derived for these solvents, for which no C_j can be calculated until they are studied in more reactions. Nevertheless, many other solvents would be expected to have *A* and *B* constants close to those for solvents that we have evaluated, e.g., 1,1,1-trichloroethane close to CCl_4, but 1,1,2-trichloroethane close to CH_2Cl_2.

4. Scope. Although linear free energy relationships are marvelously successful and versatile, each does have its limitations. Probably the best way to discover them is to apply each equation to several hundred increasingly diverse additional reactions to see where it begins to fail. We have done this for eq 2, which has two constants per solvent, and have found four reasons for misfits.

First, *misfits occur when the measured effects are not solvent effects at all because the solvent is not changed.* An example cited above under Reaction Constants is the failure of Gutmann's donor number DN to correlate well with *A* and *B*. There we suggested four sufficient reasons for the failure, the first of them being that these are not solvent effects because the solvent was always the same ($ClCH_2CH_2Cl$). If Gutmann had studied complexing between a single Lewis acid and a single base in different solvents instead of complexing with a Lewis acid in $ClCH_2CH_2Cl$ only, the resulting solvent effects might have correlated well with *A* and *B*.

A second possible cause of poor fits is *impure solvents.* Solvents like 1,2-dichloroethane may contain traces of HCl. Esters may hydrolyze slightly to acids. Acetone can form water as a result of aldol condensations, on standing or under acid or base catalysis during a reaction. On the other hand, in the absence of such catalysis, dry solvents like acetonitrile, nitromethane, and ketones may contain significantly more or less of the aci or enol tautomer than corresponds to equilibrium, owing to previous purification steps. Ethers may develop peroxides by autoxidation on standing. "Hexane" is generally a difficultly separable mixture of several isomers of hexane, predominantly *n*-hexane, with methylcyclopentane. For that reason we made *n*-heptane our reference instead, because it is more easily obtained pure. For chloroform, the constants are less well defined than for other solvents because investigators have been particularly negligent about removing the 0.75% ethanol usually present in reagent chloroform as an autoxidation inhibitor; since most have left it in, *A* and *B* are probably

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(77) For *a*, *b* and *c*, solve eq 17–19 of ref 63 once or use the solutions given as eq 4–6 under Software. For *A* ($=x_j$) and *B* ($=y_j$), solve eq 20 and 21 once. Make sure that the new data are in the same units and measured in the same direction from the same reference solvent as those in Tables I and II.

(78) Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5980.

(79) Smith, S. G.; Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1961**, *83*, 619. Reference 6, pp 233, 235–236.

(80) Menschutkin, N. A. *Z. Phys. Chem.* **1890**, *6*, 41. The effects of additives on rates and equilibria in esterification reactions recorded earlier by P. E. M. Berthelot and L. Pean de St.-Gilles in 1862–1863 were mostly dilution (concentration) effects rather than solvent effects, because rate constants and equilibrium constants were not yet recognized.

(81) Reference 8a.

(82) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7660.

(83) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 1609.

(84) Reference 83, p 1610.

(85) Smith, S. G.; Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1961**, *83*, 621. Diaz, A.; Lazdins, I.; Winstein, S. *Ibid.* **1968**, *90*, 6547.

(86) Kevill, D. N.; Kolwyck, K. C.; Weitl, F. L. *J. Am. Chem. Soc.* **1970**, *92*, 7300.

better for this mixture than for pure $CHCl_3$. A datum for one solvent may also be wrong if it was never measured but only extrapolated to pure solvent from mixtures with another solvent or to this temperature from other temperatures. Extrapolations are generally more risky than interpolations. A datum determined by another group of investigators may not be comparable due to unrecognized differences in units, conventions for including or excluding 2.303, solvent purification, or temperature control. A single seriously erroneous datum due to a solvent impurity or one of these other causes may sometimes become evident through a squared deviation more than nine times the average for all the data, in spite of the tendency of least squares to adjust the fit to avoid such large deviations.

A third reason for failure is changing the reaction at the same time as the solvent. For example, a reaction series comprised of autoprotolysis constants[68] for EtOH, MeOH, H_2O, CH_3CO_2H, and HCO_2H does not correlate well with A and B because now the identity of reactants and products are changing as well as the identity of the solvent. Compare this series with a Menschutkin reaction, $i = 23$, which does correlate well, $Et_3N + EtI \rightarrow Et_4N^+ + I^-$. Here we are concerned with a $\Delta\Delta G^{\ddagger}$ that is the difference between solvent effects $\Delta G^{\ddagger}$ on the transition state $Et_3N^{\delta+} \cdots Et \cdots I^{\delta-}$ and solvent effects ΔG on the reactants, $Et_3N + EtI$. As we change the solvent, the identities of these species do not change, although more polar and more basic solvents do stabilize the transition state relatively more and cause it to come slightly earlier (with longer N–C, shorter C–I, smaller fractional charges).[74] On the other hand, in the autoprotolysis reaction, when we go from ethanol to acetic acid, we are changing not only the solvent but also the reaction from $2EtOH \rightleftarrows EtOH_2^+ + EtO^-$ to $2AcOH \rightleftarrows AcOH_2^+ + AcO^-$, leaving practically nothing unchanged. This is more than a solvent effect. Equation 2 can cope with a change in solvent in a constant reaction or a change in reaction in a constant solvent, but it generally fails if both are changed. Neither should we expect an equilibrium such as $C_6H_5NH_2$ + solvent $\rightleftarrows$ $C_6H_5NH_3^+$ + solvent conjugate base to fit in different solvents because now one reactant and one product also change whenever the solvent changes.

How, then, is it ever possible for a solvolysis to fit? A sensible rationalization for most of the solvolyses (secondary and tertiary RX, $i = 5$–16) is that the rate-determining step is usually $RX \rightarrow R^+X^-$. Therefore, to a first approximation, the identities of the reactants and transition state do not change with solvent. Covalent bonding of solvent to R is even less at the transition state than in the Menschutkin reaction.

When R is primary ($i = 1$–4), as for solvent + CH_3Br $\rightarrow$ methylated solvent$^+$ + Br^-, it is admittedly surprising that the fit is still good in spite of heavy B involvement of most solvents, but the saving grace in these reactions may be the feature that their transition states are relatively early (reactant-like) because the products are stabler than the reactants. Although the transition states for solvolyses of CH_3Br must be significantly later than those in Menschutkin reactions, they are probably still less than halfway from reactants to first products (CH_3OHR^+) because the ratio of solvolytic rates in water and ethanol is only 27 for CH_3Br vs. 335 000 for *tert*-butyl chloride.

On the other hand, when the transition state is late, with covalent bonding to solvent that is more than half complete, one can no longer consider that the reaction is constant from one solvent to another. The reaction then changes when the solvent changes because the solvent is a major reactant. That is evidently the reason for the relatively poor fits for solvolyses of benzoyl, picryl, and phenacyl halides. Presumably each involves preliminary addition of solvent to an sp^2 carbon to give an unstable tetrahedral intermediate. The transition state immediately preceding or following the intermediate is closer in structure to the intermediate than to the original halide, i.e., involves strong bonding to the solvent, well beyond the bounds of solvation or what can be accounted for by B, our measure of the solvent's cation-solvating tendency. As a simple rule of thumb, if the solvent is not in the equation that one normally writes for the reaction that yields the data, we expect the changes with solvent to correlate well with A and B. If the solvent is in the equation and if a covalency change involving it becomes more than half complete (in a product of an equilibrium, or the transition state of a rate-determining step, or the ground or excited state of a spectral transition), the effects of changing solvent are more than "solvent effects" and will not correlate well with A and B. However, in a sense, even such a failure can be useful. A good correlation for a nucleophilic displacement by solvent on carbon confirms an S_N1 or S_N2 mechanism. A bad correlation (C_i below 0.95) strongly indicates an addition–elimination mechanism with a tetrahedral intermediate.

The fourth reason for failure is a more subtle form of the third. The reaction observed may be different in one or more of the solvents than it is in the other solvents, changing abruptly in its rate-determining step, in the principal form of the reactants, or in some other important mechanistic respect. When this happens, it is usually evident upon scrutiny of the individual deviations because they usually follow an interpretable and sensible pattern. For example, solvolysis of *tert*-butyldimethylsulfonium ion is abnormally slow in acetic acid, presumably because of a change in rate-determining step from $(CH_3)_3C^+$ formation in more polar solvents to reaction of this cation with acetic acid in acetic acid.[87] In a second example, the IR stretching frequencies of CH_3OD fit well enough in the more polar solvents, but in less basic and less polar solvents the shifts with changing solvent are less than expected. Evidently CH_3OD stops associating predominantly with the solvent and begins to self-associate because it is then a better base than the solvent. Deviations occur exactly where expected and are perfectly understandable. In a third example involving a strong electron-acceptor reactant, we found that solvents including nitrobenzene and saturated or chlorinated hydrocarbons were perfectly normal but benzene was far out of line, presumably because it complexed with the reactant, thereby modifying its reactivity.

It is surprising that such complications due to changing the state of the reactants or nature of the reaction do not occur more often because the change from water to heptane or from HMPA to TFA represents an enormous change in the environment. We believe that most of the misfits that we have found are misfits for this fourth reason. It is fortunate that misfits for this reason are relatively easily spotted and interpreted and that the interpretation often provides new insight into the mechanism of the process under observation.

5. Correlation Coefficients. It is misleading and indefensible, when determining correlation coefficients by least squares, to confuse observed and predicted data or to fail to correct for small sample size. In the simplest sort of least squares, using ROSE, the coefficient C_i for reaction i is the square root of the following determination coefficient:

$$C_i^2 = 1 - \left(\frac{\sum (z_{ij} - p_{ij})^2}{nj_i - 2} \Big/ \frac{\sum (z_{ij} - \bar{z}_i)^2}{nj_i - 1} \right)$$

Here the sums include only the nj_i terms for which observed data z_{ij} exist, $\bar{z}_i$ is the mean of observed data, p_{ij} is a predicted datum from eq 1, $nj_i - 2$ recognizes that two degrees of freedom are lost in fixing a_i and c_i in eq 1, and $nj_i - 1$ recognizes that one degree is lost in determining $\bar{z}_i$. The z_{ij} values should be observed ones, never predicted or based on secondary standards. On the other hand, p values should be as free from observed data as possible. If both p and z values were observed or partly observed, C_i could be spuriously high. If both were predicted or partly predicted, C_i would also be too high because $nj_i - 2$ would include reactions not actually observed for the reaction i in question. It is the difference between observation and prediction that is being tested, and any blurring of this distinction deceptively improves the fit. Unfortunately it is common practice to use secondary standards to supplement observed data z_{ij} and to ignore lost degrees of freedom.

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[87] Reference 71. If more basic solvents had been used, abnormally fast reactions might have been found due to incursion of an E2 mechanism.

It is our policy to use only observed data for a single reaction i for z_{ij}. We may change units (by consistent multiplication by a positive or negative integer power of 10), change sign, and subtract out the datum for a reference solvent, but we never replace z values by values predicted or calculated from other reactions or values that are averages, differences, or other combinations of data from two or more reaction series. We also use the correct number of degrees of freedom when calculating a correlation coefficient C or C_i.

In any linear least-squares extension of eq 2 to other reactions, the $nj_i - 2$ in C_i^2 is replaced by $nj_i - 3$ because three degrees of freedom are lost in fixing a_i, b_i, and c_i. In our nonlinear least-squares DOVE analysis, the situation is more complicated because solvent constants are being determined as well as reaction constants. The correct expression for the overall C (for all 77 reactions) has been given.[63] It has $1080 + 6 - (3 \times 77) - (2 \times 61) = 733$ degrees of freedom. Weights to remove the effect of different units and ranges in different reactions are also incorporated, as previously described,[63] although this lowers our overall C. The degrees of freedom for individual reactions must add up to this 733 instead of $1080 - (3 \times 77) = 849$ to keep C and C_i values comparable. Therefore, we use $(nj_i - 3)733/849$ instead of $nj_i - 3$ for C_i and similarly $(ni_j - 2)733/958$ instead of $ni_j - 2$ for C_j, although these corrections lower all C_i and C_j.

Solvent Effect Equations with Three or More Constants per Solvent

In view of the success of eq 2, these seem to be no longer needed. This conclusion is supported by the attempt by Kamlet and Taft[88] to obtain a better fit by use of more independent solvent properties.

They used a five-term equation (eq 3). Here the Greek letters

$$p_{ij} = s_i\pi_j^* + s_i d_i\delta_j + a_i\alpha_j + b_i\beta_j + c_i \qquad (3)$$

represent solvent properties, π^* for dipolarity, δ a factor for polarizability, α for hydrogen-bonding acidity, and β for hydrogen-bonding basicity. (This follows an approach pioneered by Koppel and Palm[89] at Tartu State University in Estonia. Professor Palm's journal, *Organic Reactivity*, has also published a prodigious amount of useful Russian data on solvent effects and substituent effects.) However, π^*, α, and β were each evaluated by Kamlet and Taft from a difference or other combination of two or more reaction series, and δ was arbitrarily assigned different values for different classes of solvents. In 23 publications totaling 269 journal pages, they give convenient references to many solvent-sensitive reactions and apply their eq 3 and its corollaries to them.

A quantitative comparison with our results is possible because their analyses include 18 of the 77 reactions that we studied (i = 42–44, 54–60, 62, 64–69, and 77). For two reasons their correlation coefficients might be expected to be higher than ours. First, they had the option of using any or all of four different solvent constants in eq 3, whereas we have only two in eq 2. Second, they did not retain any data that we excluded but in fact omitted from important reactions many solvents that we retained, especially extreme solvents, presumably to improve their fits.[60] For $i = 42$, our 21 solvents give $C_i = 0.984$, their 10 give 0.987; for $i = 58$, our 47 solvents give $C_i = 0.984$, their 31 give 0.985; for $i = 60$, our 34 solvents give $C_i = 0.986$, their 23 give 0.983; for $i = 68$, our 28 solvents give $C_i = 0.991$; their 16 give 0.988. For the 18 reactions, our 365 data give an overall C of 0.987, but their 279 data give 0.984. Thus use of such additional solvent parameters or different solvent parameters does not improve the fit, in spite of selective deletion of many data.

Their π^* and α parameters are significantly correlated with one another. Simple linear correlation of π^* vs. α gives calculated $\pi^* = 0.63\alpha + 0.40$ and $C = 0.52$. In contrast, our A and B are completely uncorrelated (with C imaginary). The π^* parameter is a hybrid or blend (linear combination) of A and B. Although it is our policy in general not to analyze synthetic calculated functions that are differences or averages of data from two or more reactions, we have done so with π^* and α to clarify what kind of mixtures or hybrids they represent. The following are our sensitivities a and b and correlation coefficient C. For π^*, $nj = 44$, $a = 0.298$, $b = 0.865$, $C = 0.955$. Thus π^* is roughly similar to our polarity, $A + B$ ($a = 1$, $b = 1$). It is even closer in a/b ratio to the Menschutkin reactions. As expected, it correlates well with these and many other reactions that have similar a/b ratios. For α, $nj = 7$ (best 7), $a = 1.80$, $b = -0.64$, $C = 0.998$. The α parameter closely parallels data for $i = 51$ (UV of benzophenone) and correlates well with other reactions that have high a and low b, i.e., not only with those that involve hydrogen bonding. Correlations of reactions with β are generally unsatisfactory, nor does β improve fits when included in eq 3. The parameter β is superfluous because any two different hybrids suffice, since only two underlying solvent factors (A and B) are involved. No α or β values are listed for the important extreme solvents *n*-butylamine, aniline, formic acid, and trifluoroacetic acid, all but seven α values are considered uncertain, and no β is listed for acetic acid.

Their studies are valuable in five ways: (1) they confirm that rates of Menschutkin reactions and S_N2 solvolyses of simple primary halides can be fitted just as closely as S_N1 solvolyses of tertiary halides or electronic absorption spectra if two solvent characteristics are taken into account; (2) they show that three or more solvent constants are superfluous, since the fits with two constants are already satisfactory ($C > 0.98$) and the additional constants that they tried yield no significant improvement; (3) their studies show that correlation coefficients C_i using π^* and α are closely similar to ours using A and B instead for the same reactions, although C_i values from A and B are usually a little higher because A and B are based more broadly (on 61 reactions) rather than on only one or two pairs of reactions; (4) the similarity between α and A indicates that both represent anion-solvating ability broadly rather than only hydrogen-bonding acidity, showing that hydrogen bonding does not have to be segregated and considered separately; (5) the fact that their "dipolarity" π^* is roughly a linear function of $A + 2.9B$ reveals that it is a blend or mixture of A and B and is therefore in this sense similar to our "polarity" $A + B$ and to the "solvent ionizing power" Y, which is a linear function of $A + 0.8B$, and to log k_2 for EtI + Et_3N at 25 °C, which is a linear function of $A + 4.7B$.

Conclusion

Two unrelated solvent properties (A and B) alone account for over 98% of the effects from changing solvent in a set of 1080 typical rates, equilibria, and spectral energies that we examined. Ordinary multiple least squares can be used to evaluate the corresponding properties (A and B) of other solvents from these reactions or to evaluate the sensitivities (a and b) of other reactions to these solvent properties. A measures anion-solvating tendency, and B measures cation-solvating tendency. They are nearly equally important in solvolyses of *tert*-butyl chloride. Points of mechanistic change in reactions can often be detected by noting where their solvent effects would first require a new a and b to fit.

Experimental Section

Spectra. Table X records wavelengths of UV absorption maxima for 3-methoxypyridine *N*-oxide (I) in 17 solvents, measured with a Zeiss PMQII spectrophotometer. Three bands are found. The data for acetic acid ($j = 14$) were not used because I may be significantly protonated in this solvent. I was prepared by refluxing 3-chloropyridine *N*-oxide overnight with a solution of sodium methoxide in methanol;[90] mp 100–101 °C after two crystallizations from acetone-ether (lit.[90] mp 100–102 °C). Triethylamine and reagent tetrahydrofuran were stored over Drierite ($CaSO_4$) overnight and then distilled. Other solvents were reagent or spectral grade. The spectrum of I in 1,4-dioxane was not changed when the solvent contained 0.1% water by volume; a small shift was observed with 1% water.[91]

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(88) For references to 23 papers from 1976 to 1981 by Kamlet and Taft, see: Chawla, B.; Pollack, S. K.; Lebrilla, C. B.; Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 6924. Kamlet, M. J.; Carr, P. W.; Taft, R. W.; Abraham, M. H. *Ibid.* **1981**, *103*, 6062. Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485–630.

(89) Koppel, I. A.; Palm, V. A. *Org. React.* (*Tartu*) **1967**, *4*, 862, 892; **1971**, *8*, 296. Reference 6, pp 256–260.

(90) Katritzky, A. R.; Beard, J. A. T.; Coats, N. A. *J. Chem. Soc.* **1959**, 3683.

Table X. Absorption Maxima in nm at 25 °C for Solutions of 3-Methoxypyridine *N*-Oxide[39] (i = 45–47) in 17 Solvents j

j	λ_1	λ_2	λ_3
1	315.25	283.5	
3	309.5	276.5	233.75
7	299.0	263.0	224.0
12	309.75	275.0	231.75
13	311.25	277.25	
14	293.0	253.75	
15	300.0	265.0	224.5
16	310.5	276.75	
19	311.5	277.25	
24	314.25	277.5	
25	313.5	278.5	
28	318.0	279.0	235.0
30	313.25	277.5	
36	316.0	280.25	
41	319.25	280.0	
53	321.75	279.75	236.0
55	294.5	254.75	220.0

Hardware. Programs were run on the M.I.T. Information Processing Service's Honeywell Multics 68/DPS computer by using its ANSI77 Fortran compiler. Tables II–VII were printed from the computer's disk storage by an IBM 6670 or Xerox 9700 printer. The figures were plotted by the computer by Multics graphics, Figure 1, on a Tektronix 4610 hardcopy unit attached to a Tektronix 4013 CRT scope, Figure 2, on a CalComp 905 plotter.

Software. The DOVE procedure has been described.[63] Our program is coded in Fortran 77, in accord with the ANSI 1978 full language standard.[92] It consists of a main program of 1084 statements (in 984 lines) and no subprograms. It embodies options, selected by a line of control variables initially read in, for linear least squares by eq 1 (ROSE), nonlinear least squares by eq 1 (LOVE), nonlinear least squares by eq 2 (DOVE), or multiple linear least-squares extensions by eq 2 (RIXY for new reactions, NEWS for new solvents). It incorporates our Monte Carlo method (UNCERT)[65] for calculating the uncertainty (standard deviation) of each calculated constant. It uses our random number generator (URN)[93] for initial values of the constants and for the Monte Carlo error analysis. In the solvent problem, about one-third of the random number sets from URN for initial values of the constants lead to convergence, always with same 353 final constants, in 600 cycles or less; convergence is much slower with <200 data than with 1080. All real numbers are double precision (about 18 decimal places on Multics). Correlation coefficients are calculated with the correct numbers of degrees of freedom.[61] The subsidiary conditions for DOVE were incorporated by a transformation after each cycle. Observed data z can be entered by a list-directed reading of either Table II or a less compacted file. Data were compacted to produce Tables II and VII on disk by a separate program called SQUASH. Other options of our DOVE program provide data for other programs for other computer-generated outputs: for FIG, which produced Figure 1, for DVPLT, which produced Figure 2, and for TAB, which produced Tables III–VI. The DVPLT program, which generated Figure 2, uses an M.I.T. Information Processing Services subroutine called SCALE1, which is better than the standard CalComp routine SCALE because SCALE1 always scales to within 15% of an axis length of the frame. We designed and included coding for automatic labeling of points, especially for the more important solvents (j = 7, 14, 15, 55), with automatic exclusion of labels (but not points) where labels would overlap. Otherwise the subroutines called by DVPLT are standard Multics graphics subroutines identical with or compatible with those supplied by CalComp, Inc., for its plotters.

Our DOVE program is available from this journal as supplementary material, or users may recode more simply for themselves from our published descriptions of these methods.[63,65,93] However, DOVE is not needed for use of our tabulated solvent or reaction constants in further work with eq 2. That requires only ordinary multiple linear least-squares regression as described in the section entitled Extension to Other Reactions or Solvents, and such programs are relatively simple, short, and easily coded. For example, for multiple linear least squares for new reactions, the expressions for a, b, c, and corrected correlation coefficient C_i reduce to eq 4–7:

$$a = (GQ - EH)/(GG - DE) \tag{4}$$

$$b = (H - aD)/G \tag{5}$$

$$c = (\sum z - a\sum A - b\sum B)/n \tag{6}$$

$$C_i = (1 - wI/(n - 3))^{1/2} \tag{7}$$

where

$$D = n\sum A^2 - (\sum A)^2 \qquad E = n\sum B^2 - (\sum B)^2 \qquad F = n\sum z^2 - (\sum z)^2$$

$$G = n\sum AB - \sum A\sum B \qquad H = n\sum Az - \sum A\sum z$$

$$Q = n\sum Bz - \sum B\sum z$$

$$I = \sum z^2 + a^2\sum A^2 + b^2\sum B^2 + c^2 n + \\ 2(-a(\sum Az - b\sum AB - c\sum A) - b(\sum Bz - c\sum B) - c\sum z)$$

$$w = (n - 1)/\sum(z - \sum z/n)^2 = n(n - 1)/F$$

After a, b, and c are evaluated, the predicted p (eq 2) and signed relative (weighted) squared deviation (sgn $(z - p))w(z - p)^2$) for each solvent should be calculated because solvents that deviate widely often signal a change of mechanism (fourth reason under Scope).

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Registry No. 3-Methoxypyridine *N*-oxide, 14906-61-7.

Supplementary Material Available: DOVE computer program (19 pages). Ordering information is given on any current masthead page.

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(91) We began this study of solvent effects in 1973 because of our suspicion that water or alcohol impurities and solid-state (wall or surface) effects were much more influential in reactions 43, 58, and others in our group of 77 than we now believe them to be after our variations of water concentration and cell material in reactions 45–47.

(92) Programming Language Fortran, ANSI X3.9-1978; American National Standards Institute: New York, 1978. Series 60 (Level 68) Multics Fortran Manual, AT58-02; Honeywell Information Systems, Inc.: Waltham, MA, 1979.

(93) Swain, C. G.; Swain, M. S. *J. Chem. Inf. Comput. Sci.* **1980**, *20*, 56.