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Linear Solvation Energy Relationships. 6. Additions to and Correlations with the π^* Scale of Solvent Polarities[1]

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The solvatochromic comparison method is used with nine solvatochromic indicators to determine π^* values for 23 additional solvents. The expanded π^* scale of solvent polarity–polarizabilities is then used to rationalize solvent effects on rates of a Menschutkin reaction, rates of a peroxyester thermal decomposition, and free energies of transfer of a tetraalkylammonium halide between solvents. It is suggested that the excellent correlations serve as ultimate vindication of the underlying concept of linear solvation energy relationships, i.e., that when polarity, polarizability, and hydrogen bonding effects are correctly unravelled, solvents exert parallel effects on many chemical properties and reactivity parameters.

In part 6 of the Solvatochromic Comparison Method series,[3] we described the use of that method to formulate a π^* scale of solvent polarity–polarizabilities, so named because it derived from and was best fitted to correlate solvent effects on $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic spectral transitions of uncharged molecules. Solvatochromic shifts for seven mainly nitroaromatic indicators were used toward the construction of an initial scale comprising 28 solvent π^* values; this was then refined and expanded to 72 π^* values by correlations with $\nu_{\max}$ results for 40 additional indicator compounds containing many chromophore types.

In part 1 of the current LSER series,[4] we related effects on infrared spectral stretch band frequencies to solvent π^* values, and in parts 2–4[5-7] we reported additional multiple parameter least-squares correlations of spectral and reactivity data with linear combinations of solvent π^* and α or π^* and β values (from an α scale of solvent hydrogen bond donor acidities[6-8] and a β scale of solvent hydrogen bond acceptor basicities[5,9,10]). We wish now to report π^* values for 23 additional solvents, and to describe some further correlations with reactivity results.

Solvatochromic equations for the $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ spectral bands reported earlier[3] took the form

$$\nu(i)_{\max} = \nu_0 + s\pi^* \tag{1}$$

In the present study we have used nine indicator compounds, for which the least-squares fits to eq 1 showed high correlation ($r > 0.984$), to determine π^*_i values for the new solvents through the reciprocals of the earlier correlation equations, i.e.,

$$\pi^*_i = (\nu_{\max} - \nu_0)/s \tag{2}$$

The π^*_i results were then averaged to arrive at the final values of the solvent polarity–polarizability terms. The nine indicators and the equations for the π^*_i's are:

(1) *N,N*-diethyl-3-nitroaniline

$$\pi^*_1 = \frac{\nu(1)_{\max} - 25.57}{-2.212} \tag{3a}$$

(2) 4-methoxy-β-nitrostyrene

$$\pi^*_2 = \frac{\nu(2)_{\max} - 30.00}{-2.329} \tag{3b}$$

(3) *N,N*-diethyl-4-nitroaniline

$$\pi^*_3 = \frac{\nu(3)_{\max} - 27.52}{-3.182} \tag{3c}$$

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[1] Part 5: M. J. Kamlet, A. Solomonovici, and R. W. Taft, *J. Am. Chem. Soc.*, in press.

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[3] M. J. Kamlet, J. L. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 6027 (1977).

[4] M. J. Kamlet and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 337 (1979).

[5] M. J. Kamlet, J. L. Abboud, M. E. Jones, and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 342 (1979).

[6] R. W. Taft and M. J. Kamlet, *J. Chem. Soc., Perkin Trans. 2*, in press.

[7] M. J. Kamlet and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 349 (1979).

[8] R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, **98**, 2886 (1976).

[9] M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 377 (1976).

[10] T. Yokoyama, R. W. Taft, and M. J. Kamlet, *J. Am. Chem. Soc.*, **98**, 3233 (1976).

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(4) 4-nitroanisole

$$\pi^*_4 = \frac{\nu(4)_{\max} - 34.17}{-2.410} \qquad (3d)$$

(5) *N,N*-diethyl-3-methyl-4-nitroaniline

$$\pi^*_5 = \frac{\nu(5)_{\max} - 27.67}{-3.073} \qquad (3e)$$

(6) *N,N*-dimethyl-4-nitroaniline

$$\pi^*_6 = \frac{\nu(6)_{\max} - 28.10}{-3.436} \qquad (3f)$$

(7) *N,N*,3,5-tetramethyl-4-nitroaniline

$$\pi^*_7 = \frac{\nu(7)_{\max} - 27.36}{-2.747} \qquad (3g)$$

(8) 4-dimethylaminobenzophenone

$$\pi^*_8 = \frac{\nu(8)_{\max} - 30.41}{-2.013} \qquad (3h)$$

(9) 4,4′-bis(dimethylamino)benzophenone

$$\pi^*_9 = \frac{\nu(9)_{\max} - 29.96}{-2.094} \qquad (3i)$$

The $\nu_{\max}$ and π^*_i values for the nine indicators in the 23 solvents are assembled in Table I, together with "best estimates" of π^*, obtained by throwing out the high and low π^*_i values for each solvent and averaging the remainder.[11]

Correlations with Reactivity Data. Where hydrogen-bonding effects are excluded, as when neither solvents nor solutes are hydrogen-bond donors, solvatochromic equations[12] can take either of two forms. For $p \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ spectral transitions, with all solvents considered together (as for the indicators discussed above), and for other properties if families of solvents with similar polarizability characteristics are considered separately[13] (e.g., only nonchlorinated aliphatic solvents, only polychlorinated aliphatics, or only aromatic solvents), the form of the equations is

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s\pi^* \qquad (4)$$

For other XYZ's, if all solvents need to be considered together, the equation becomes

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s'(\pi^* + d\delta) \qquad (5)$$

where δ, a polarizability correction term, is 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents.[14] The XYZ property in eq 4 and 5 may be a position or intensity of maximal absorption in a UV, IR, NMR, or ESR spectrum, a free energy or heat of solution or of transfer between solvents, or the logarithm of a rate or equilibrium constant or of a fluorescence lifetime.

The most extensive single-source set of accurate reactivity data in pure single solvents in the chemical literature is for the Menschutkin reaction of tri-*n*-propylamine with methyl iodide at 20 °C.

$$(n\text{-}\mathrm{C_3H_7})_3\mathrm{N} + \mathrm{CH_3I} \xrightarrow{k(6)} (n\text{-}\mathrm{C_3H_7})_3\overset{+}{\mathrm{N}}\mathrm{CH_3}\ \mathrm{I}^- \qquad (6)$$

Lassau and Jungers[15] have reported rate constants for this reaction in 78 solvents. Of these, 70 are non-hydrogen-bond donors (or have α values below 0.2),[6-8] so that hydrogen-bonding effects were essentially eliminated.[16] Values of π^* have now been determined for 44 of these solvents.

An all-data least-squares fit of the 44 log $k(6)$ results and corresponding solvent π^* values to eq 4 leads to the correlation equation,

$$\log k(6) = -4.24 + 4.43\pi^* \qquad (7)$$

with r (the correlation coefficient) = 0.981, and SD (the standard deviation) = 0.21 log unit. Although these measures of the goodness of the linear fit are satisfactory by the standards usually applied to linear free-energy relationships, statistically significant improvements in r and SD are observed when the correlations are limited to families of solvents with similar polarizability characteristics. Thus, for 15 nonchlorinated aliphatic solvents, the regression equation becomes

$$\log k(6) = -4.38 + 4.98\pi^* \quad r = 0.994, \quad \mathrm{SD} = 0.16 \qquad (8a)$$

for 11 polychlorinated aliphatic solvents,

$$\log k(6) = -4.40 + 4.70\pi^* \quad r = 0.993, \quad \mathrm{SD} = 0.13 \qquad (8b)$$

and for 18 aromatic solvents,

$$\log k(6) = -4.07 + 3.98\pi^* \quad r = 0.989, \quad \mathrm{SD} = 0.12 \qquad (8c)$$

Alternatively, if the results are fitted to eq 5, the d term is calculated to be −0.086,[14] and the preferred all-data correlation equation becomes

$$\log k(6) = -4.18 + 4.66(\pi^* - 0.086\delta) \quad r = 0.988, \quad \mathrm{SD} = 0.17 \qquad (9)$$

Log $k(6)$ values are plotted against corresponding π^* values in Figure 1, and against $\pi^* - 0.086\delta$ in Figure 2. We shall report further on solvent and structural effects on Menschutkin reaction rates in terms of π^* and α values in a future paper.

Correlations with solvent π^* values are equally good, albeit based on fewer data, for the pyridine-catalyzed ionic decomposition of *tert*-butyl peroxyformate at 90 °C. Pincock has reported second-order rate constants for this reaction in 20 solvents,[17] of which 15 are of known π^*.

$$\mathrm{O{=}CHOOC(CH_3)_3} \xrightarrow[\text{pyridine}]{k(10)} \mathrm{CO_2} + \mathrm{HOC(CH_3)_3} \qquad (10)$$

The all-data least squares fit to eq 4 is

$$\log k(10) = 0.30 + 1.96\pi^* \quad r = 0.986, \quad \mathrm{SD} = 0.11 \qquad (11)$$

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[11] We have adopted this procedure to minimize effects of hidden underlying lower intensity bands and other "spectral anomalies" such as were discussed in footnote 16 of ref 3.

[12] Although the equations have been extended to cover many nonspectroscopic properties, we find it convenient to continue to refer to the method as the solvatochromic comparison method, the equations as the solvatochromic equations, the π^*, α, β, and δ terms as the solvatochromic parameters, and the s, a, b, and d terms as the solvatochromic coefficients.

[13] J. L. Abboud, M. J. Kamlet, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 8327 (1977); J. L. Abboud and R. W. Taft, *J. Phys. Chem.*, **83**, 412 (1979).

[14] The d term is estimated through the equation $d = 2\Delta\mathrm{XYZ}/[s(\mathrm{al}) + s(\mathrm{ar})]$, where ΔXYZ is the difference between values calculated through the aliphatic and aromatic regression equations at $\pi^* = 0.7$, and s(al) and s(ar) are the slopes of those regression equations.

[15] C. Lassau and J.-C. Jungers, *Bull. Soc. Chim. Fr.*, 2678 (1968).

[16] We shall report in a future paper that type A hydrogen bonding (the solvent acts as HBD acid) has two offsetting effects on Menschutkin reactions. By hydrogen bonding to the attacking trialkylamine nucleophile, protic solvents decelerate the reaction; by hydrogen bonding to the leaving halide ion (electrophilic assistance) they accelerate the reaction. Examples are available where either effect dominates.

[17] R. E. Pincock, *J. Am. Chem. Soc.*, **86**, 1820 (1964).

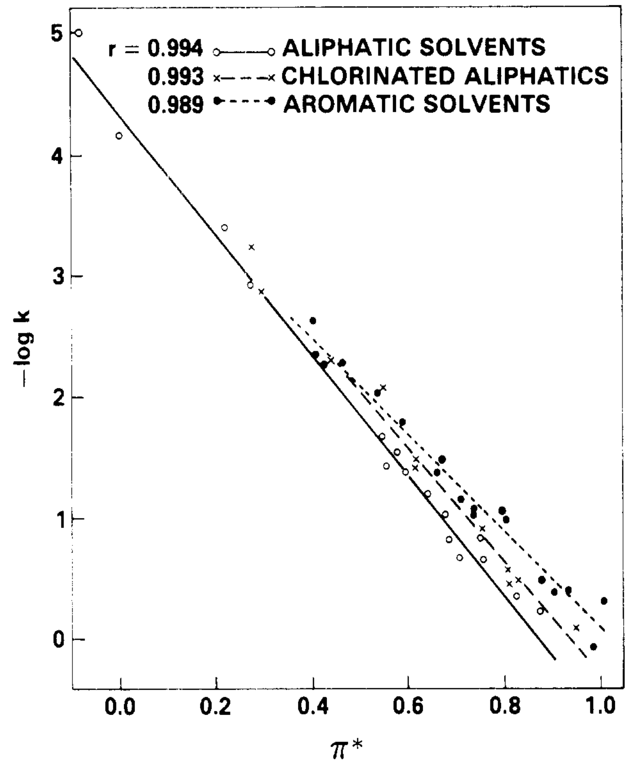

Figure 1. Log $k(6)$ for the Menschutkin reaction of tripropylamine with methyl iodide plotted against solvent π^* values.

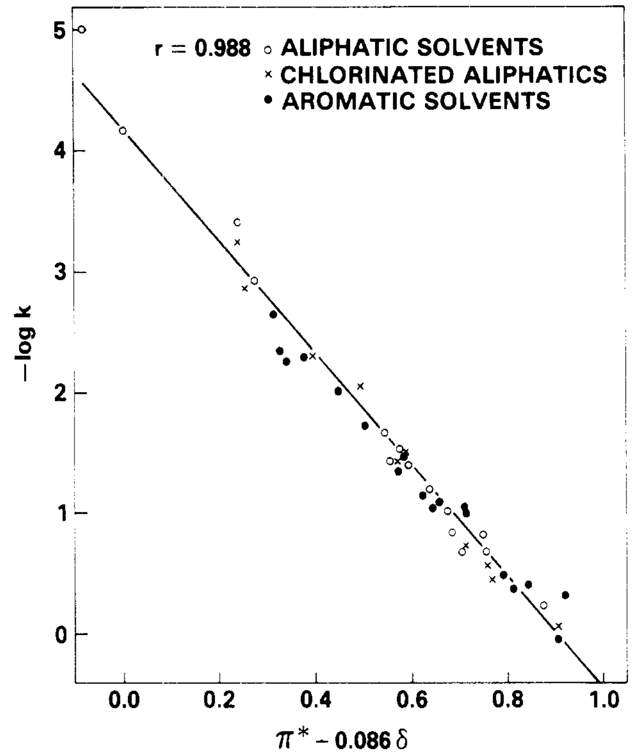

Figure 2. Log $k(6)$ plotted against $\pi^* + d\delta$.

Again the excellent correlation becomes even better when families of solvents with similar polarizability characteristics are considered separately. Thus, for six aliphatic solvents, the regression equation is

$$\log k(10) = 0.32 + 2.12\pi^* \qquad r = 0.994, \quad SD = 0.09 \tag{12a}$$

and for six aromatic solvents,

$$\log k(10) = 0.25 + 2.00\pi^* \qquad r = 0.983, \quad SD = 0.09 \tag{12b}$$

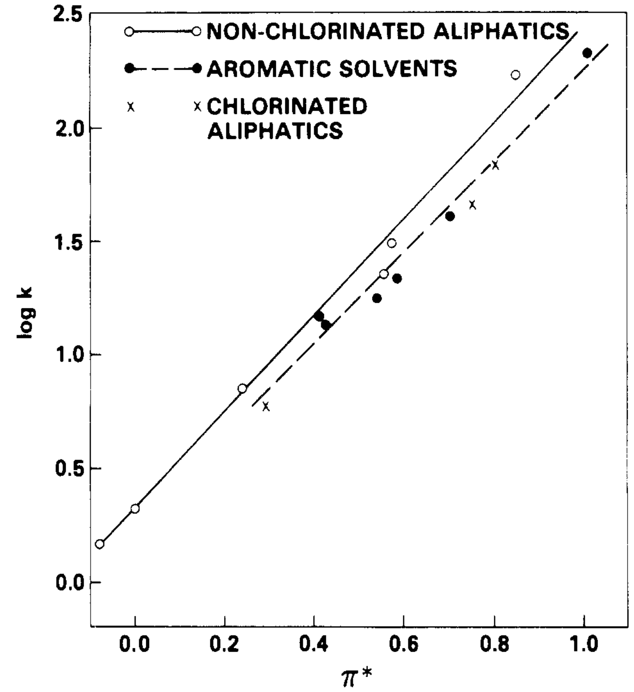

Figure 3. Log $k(10)$ for the pyridine-catalyzed ionic decomposition of *tert*-butyl peroxyformate plotted against solvent π^* values.

Finally, the d term is calculated to be −0.074,[14] and the all-data fit to eq 5 is

$$\log k(10) = 0.32 + 2.05(\pi^* - 0.074\delta) \qquad r = 0.989, \quad SD = 0.09 \tag{13}$$

The log $k(10)$ results are plotted against corresponding solvent π^* values in Figure 3.

Free Energies of Transfer of $Et_4N^+I^-$. Another somewhat different set of properties which is well correlated by the π^* parameter involves the free energies of transfer of the tetraethylammonium iodide ion pair from methanol to various other solvents. Abraham[18] has reported 34 ΔG_t^c values, of which 21 are for nonhydrogen bond donor solvents whose π^* values are known.

The all-data least-squares fit of Abraham's results to eq 4 gives the regression equation

$$\Delta G_t^c = 12.79 - 12.51\pi^* \text{ kcal/mol} \qquad r = 0.954, \quad SD = 0.92 \tag{14}$$

If only the ten nonchlorinated aliphatic solvents are considered, the equation becomes

$$\Delta G_t^c = 12.48 - 13.27\pi^* \text{ kcal/mol} \qquad r = 0.985, \quad SD = 0.73 \tag{15a}$$

for five polychlorinated aliphatics

$$\Delta G_t^c = 15.57 - 16.48\pi^* \text{ kcal/mol} \qquad r = 0.990, \quad SD = 0.68 \tag{15b}$$

and for six aromatic solvents

$$\Delta G_t^c = 13.05 - 11.29\pi^* \text{ kcal/mol} \qquad r = 0.961, \quad SD = 0.58 \tag{15c}$$

The improvement in all-data correlation on inclusion of the $d\delta$ term is significantly greater for the ΔG_t^c's than for

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[18] M. H. Abraham, *J. Chem. Soc., Perkin Trans. 2*, 1343 (1972).

[19] Methyl formate (solvent **99**) has been excluded from the correlation. It may be noted that **99** also fell out of line in the π^* vs. dipole moment correlation reported earlier.[13] It was suggested that this was because **99** is a solvent of small steric requirements.

Table I. Amendment and Extension of the π^* Scale of Solvent Polarities[d]

no.[a]	solvent	indicator	ν_{max}	π^*_i[b]	indicator	ν_{max}	π^*_i[b]	indicator	ν_{max}	π^*_i[b]	π^*_{ave}[b]
34	acetic anhydride	1	23.36	(0.976)	4	32.41	0.730	7	25.22	0.779	0.756 ± 0.024
		2	28.48	(0.652)	5	25.28	0.784	8	28.93	0.736	
		3	25.03	0.784	6	25.40	0.785	9	28.38	0.755	
88	bis(2-methoxyethyl) ether	1	24.09	0.647	4	32.52	(0.685)	7	25.52	0.670	0.640 ± 0.017
		2	28.51	0.640	5	25.59	0.651	8	29.22	0.593	
		3	25.45	0.651	6	25.94	0.629	9	28 73	(0.589)	
89	butyronitrile	1	24.00	0.687	4	32.55	0.672	7	25.34	0.736	0.706 ± 0 027
		2	28.56	(0.618)	5	25.40	(0.745)	8	29.05	0.677	
		3	25.16	0.742	6	25.57	0.736	9	28 51	0.672	
90	cumene	1	24.63	0.402	4	33.07	(0.456)	7	26.24	0.410	0.410 ± 0.010
		2	29.00	0.430	5	26.47	0.397	8	29.56	0.422	
		3	26.27	0.393	6	26.68	0.413	9	29.15	(0.389)	
91	1,2-dibromoethane	1	23.85	0.755	4	32.35	0.755	5	25.44	(0.700)	0.751 ± 0.020
		2	28.18	0.782	5	25.44	0.732	6	28.81	(0.794)	
		3	25.19	0.732	6	25.63	0.719	7	28.32	0.784	
92	*m*-dichlorobenzene	1	24.06	0.660	4	32.53	0.680	7	25.60	0.640	0.670 ± 0.023
		2	28.26	(0.747)	5	25.67	0.657	8	28.98	0.708	
		3	25.48	0.641	6	25.96	(0.632)	9	28.49	0.701	
93	*trans*-1,2-dichloroethylene	1	24.48	0.470	4	33.28	(0.370)	7	26.34	0.371	0.440 ± 0.044
		2	28.91	0.468	5	26.10	(0.517)	8	29.59	0.410	
		3	25.94	0.497	6	26.45	0.480	9	29.15	0.387	
94	diethyl malonate	1	24.13	0.628	4	32.63	0.639	7	25.51	(0.673)	0.637 ± 0.016
		2	28.54	0.627	5	25.65	0.664	8	29.18	0.612	
		3	25.41	0.663	6	25.95	0.626	9	28.70	(0.603)	
95	ethyl acetoacetate	1	23.87	0.746	4			7	25.26	0.765	0.751 ± 0.019
		2	28.34	0.714	5	25.30	(0.778)	8	28.93	0.734	
		3	25.05	0.776	6	25.84	(0.659	9	28.35	0.769	
96	ethyl trichloroacetate	1	24.35	(0.530)	4	28.13	0.595	7	25.69	0.607	0.611 ± 0.009
		2	28.59	0.605	5	29.64	0.634	8	28.91	(0.745)	
		3	25.57	0.614	6	26 01	0.608	9			
97	fluorobenzene	1	24.15	0.619	4	32 49	(0.696)	7	25.65	0.621	0.622 ± 0.004
		2	28.54	0.626	5	25.76	0.628	8	29.16	0.623	
		3	25.53	0.625	6	25.99	0.614	9	28.68	(0 610)	
98	3-heptanone	1	24.20	0.597	4			7	25.66	0.618	0.592 ± 0.030
		2	28.73	0.545	5	25.75	(0.631)	8	29.30	0.549	
		3	25.53	0.625	6	25.98	0.617	9	28.82	(0.544)	
79	2,6-lutidine	1	24.08	0.651	4	32.49	(0.698)	7	25.56	0 656	0.660 ± 0.010
		2	28.39	0.693	5	25.69	0.650	8	29.09	0.656	
		3	25.50	(0.635)	6	25.84	0.657	9	28.59	0.654	
52	methyl acetate	1	24.37	0.520	4	32.89	0.531	7	25.77	0.579	0.528 ± 0.039
		2	28.92	0.463	5	25.91	(0.579)	8	29.46	0.473	
		3	25.75	0.556	6	26.14	0.570	9	29.00	(0.460)	
99	methyl formate	1	24.22	0.588	4	32.76	0.585	7	25 55	0.660	0.605 ± 0.027
		2	28.80	(0.516)	5	25.66	(0.660)	8	29.24	0.583	
		3	25.45	0.650	6	25.89	0.643	9	28.74	0.583	
130[c]	methylal	1	24.79	0.330	4	33.31	0.357	7	26.29	0.390	0.353 ± 0.030
		2	29.30	(0.301)	5	26.48	(0.394)	8	29.77	0.317	
		3	26.33	0.374	6	26.75	0.393	9	29.32	0.307	
131	phenylacetone	1	23.53	0.900	4			7	25.00	(0.859)	0.879 ± 0.009
		2			5	25.01	0.872	8	28 66	0.868	
		3	24.74	0.874	6	24.99	(0.905)	9	28.12	0.880	

63	phenylacetonitrile	1	23.38	0.988	4	31.95	(0.921)	7	24.76	0.948	0.988 ± 0.025
		2	27.71	0.983	5	24.75	0.967	8	28.37	1.016	
		3	24.51	0.966	6	24.86	0.943	9	28.36	(1.018)	
132	pentachloroethane	1	24.16	0.614	4	32.72	0.602	7			0.618 ± 0.010
		2	28.50	(0.646)	5	25.74	0.633	8			
		3	25.54	0.622	6	26.07	0.591	9			
56	sulfolane	1	23.37	0.971	4	31.91	(0.940)	7	24.66	0.982	0.977 ± 0.014
		2	27.81	0.940	5	24.67	0.982	8	28.40	0.997	
		3	24.37	0.990	6	24.67	(0.998)	9	27.99	0.942	
133	trimethyl orthoacetate	1	24.79	0.330	4			7	26 30	(0.386)	0.348 ± 0.012
		2	29.20	0.344	5	26.62	0.348	8	29.80	(0.304)	
		3	26.42	0.346	6	26.79	0.381	9	29.26	0.336	
134	trimethyl orthoformate	1	24.24	0.579	4	32.72	0.601	7	25.66	(0.618)	0.576 ± 0.032
		2	28.78	0.524	5	25.85	0.599	8	29.37	0.515	
		3	25.60	0.603	6	26.01	0.608	9	28.89	(0.509)	
135	*m*-xylene	1	24.55	0.439	4	32.99	0.490	7	26.00	0.495	0.464 ± 0.026
		2	28.84	0.498	5	26.38	0.426	8	29.51	0.450	
		3	26.18	(0.421)	6	26.56	0.448	9	28.88	(0.516)	

[a] Solvent numbering is the same in all papers of this series. [b] High and low values (in parentheses) are excluded from the average. [c] Numbers **101-130** reserved for ROH solvents. [d] Electronic spectral data in 10^{-3} cm^{-1}.

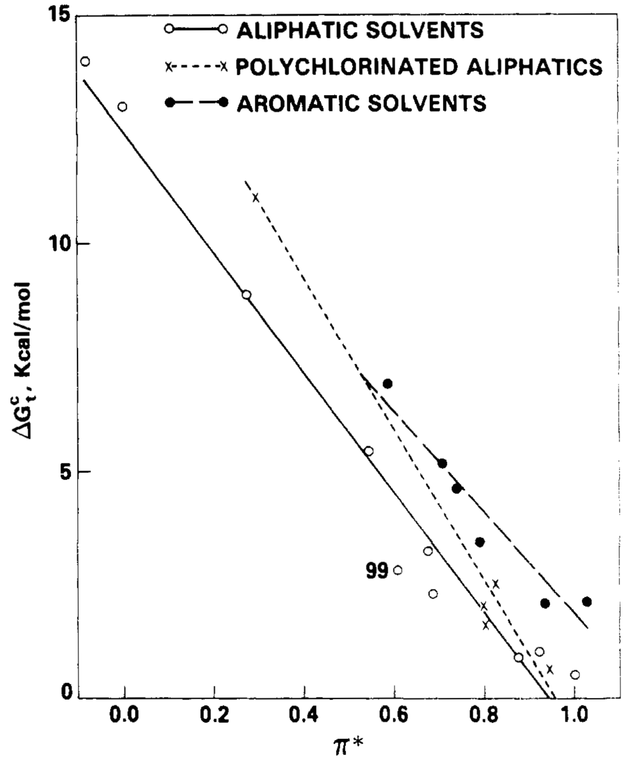

Figure 4. ΔG_t^c from methanol to a variety of other solvents for the $Et_4N^+I^-$ ion pair plotted against solvent π* values.

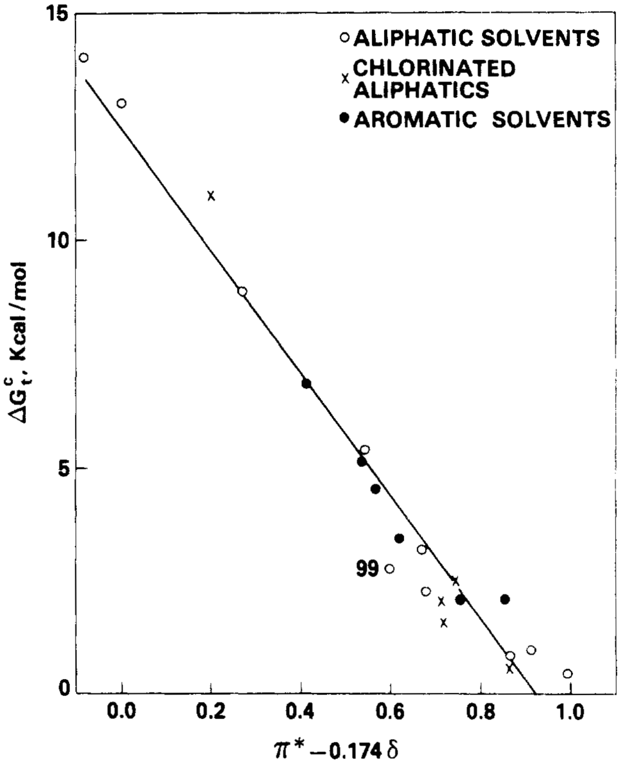

Figure 5. ΔG_t^c plotted against $\pi^* + d\delta$.

the XYZ's discussed earlier. The *d* value is calculated to be −0.174,[14] and the least squares fit to eq 5 gives

$$\Delta G_t^c = 12.67 - 13.67(\pi^* - 0.174\delta) \text{ kcal/mol}$$
$$r = 0.984, \quad SD = 0.76^{19} \qquad (16)$$

The ΔG_t^c results are plotted against corresponding solvent π* values in Figure 4 and against values of π* − 0.174δ in Figure 5.

The underlying concept in linear solvation energy relationships is that, when polarity, polarizability, and hydrogen-bonding effects are correctly unravelled, solvents exert parallel effects on many types of properties and reactivity parameters. That a solvent polarity–polarizability scale, based on electronic spectra, is successful in correlating such disparate properties as rates of a Menschutkin reaction, rates of a peroxyester decomposition, and free energies of transfer of a tetraalkylammonium halide between solvents seems an ultimate vindication of this concept.

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Registry No. Acetic anhydride, 108-24-7; bis(2-methoxyethyl) ether, 111-96-6; butyronitrile, 109-74-0; cumene, 98-82-8; 1,2-dibromoethane, 106-93-4; *m*-dichlorobenzene, 541-73-1; *trans*-1,2-dichloroethylene, 156-60-5; diethyl malonate, 105-53-3; ethyl acetoacetate, 141-97-9; ethyl trichloroacetate, 515-84-4; fluorobenzene, 462-06-6; 3-heptanone, 106-35-4; 2,6-lutidine, 108-48-5; methyl acetate, 79-20-9; methyl formate, 107-31-3; methylal, 109-87-5; phenylacetone, 103-79-7; phenylacetonitrile, 140-29-4; pentachloroethane, 76-01-7; sulfolane, 126-33-0; trimethyl orthoacetate, 1445-45-0; trimethyl orthoformate, 149-73-5; *m*-xylene, 108-38-3; *N,N*-diethyl-3-nitroaniline, 2216-16-2; 4-methoxy-β-nitrostyrene, 3179-10-0; *N,N*-diethyl-4-nitroaniline, 2216-15-1; 4-nitroanisole, 100-17-4; *N,N*-diethyl-3-methyl-4-nitroaniline, 52177-26-1; *N,N*-dimethyl-4-nitroaniline, 100-23-2; *N,N*,3,5-tetramethyl-4-nitroaniline, 64325-04-8; 4-(dimethylamino)benzophenone, 530-44-9; 4,4′-bis(dimethylamino)benzophenone, 90-94-8; tripropylamine, 102-69-2; methyl iodide, 74-88-4; tetraethylammonium iodide, 68-05-3; pyridine, 110-86-1; *tert*-butyl peroxyformate, 819-50-1.

Substituent Effects on Reactivity in $S_{RN}1$ Reactions of Aryl Iodides with Pinacolone Enolate Ion[1]

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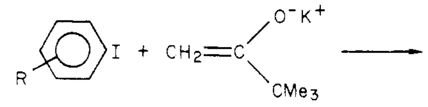
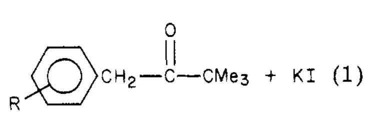
In the dark reactions of six aryl iodides with pinacolone enolate ion in dimethyl sulfoxide solution, which are believed to occur by the radical chain $S_{RN}1$ mechanism, relative reactivity varies enormously depending on the method of measurement. The maximum difference in reactivity among the six substrates *reacting separately* is nearly 400-fold, but the maximum difference *in competition* vs. bromobenzene is less than twofold. Such a huge difference is not unreasonable for radical chain reactions inasmuch as differences in initiation as well as propagation (and termination) reactivity are manifested in separate reactions whereas (if the chain is long) only differences in propagation reactivity are revealed by competition experiments. The two measures of reactivity correlate only roughly with σ substituent parameters, but they correlate better with polarographic half-wave reduction potentials or with each other.

Iodo- and bromobenzene react spontaneously in the dark at room temperature with pinacolone enolate ion to form 3,3-dimethyl-1-phenyl-2-butanone (**3a**);[3] see eq 1. Reaction is believed on the basis of good evidence to occur by the radical chain $S_{RN}1$ mechanism. Most of the known aromatic $S_{RN}1$ reactions[4] require stimulation by photons or electrons in order for reaction to occur at a conveniently observable rate. Reactions such as that of eq 1 that occur spontaneously in the dark clearly involve some thermally activated initiation process, and that makes them particularly interesting.



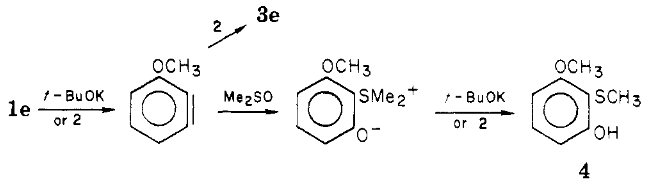
1a, R = H
b, R = p-CH_3
c, R = m-CH_3
d, R = p-OCH_3
e, R = m-OCH_3
f, R = p-F

2



3a, R = H
b, R = p-CH_3
c, R = m-CH_3
d, R = p-OCH_3
e, R = m-OCH_3
f, R = p-F

Scheme I



4

Heretofore little has been learned about reactivity in aromatic $S_{RN}1$ reactions as affected by substituents in the aromatic system. There have been a few qualitative observations that specific reactions occur satisfactorily when alkyl, alkoxy, aryl, fluoro, or carboxylate groups are present[5-7] but that they fail with substituents such as *m*-nitro and the ionized *p*-hydroxy group (O^-) as well as in the case of iodoferrocene. By competition experiments, Komin and Wolfe[8] have demonstrated the reactivity order

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(2) On sabbatical leave from Ripon College, 1975–1976.

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