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Improvements of the Empirical π^* Solvent Polarity Scale

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The famous empirical π^* (or π^*_1(N)) solvent polarity scale has been improved for nonassociating solvents by introducing newly presented solvent polarity parameters of π^*_1 and π^*_2. Here, the π^*_1 parameter is a modified form of the π^*_1(N) scale. The shortcoming that the π^* scale does not correlate to solvent spectral shifts of nonpolar and less polarized solutes has been overcome by introducing the new supplementary π^*_2 solvent scale. The present parameters of π^*_1 and π^*_2, the physical meanings of which are clarified on the basis of their theoretical background, are more successfully applied to the solvent frequencies of both nonpolar and less polarized solutes and to the logarithmic rate constants for organic reactions than is the π^*_1(N) scale.

Since 1948 many solvent polarity scales have been proposed.[1] According to Bekárex,[6] more than 50 procedures and solvent scales have been suggested hitherto in the fields of empirical and semiempirical methods concerning the present problem. The most famous empirical scales are the Grunwald and Winstein's Y values,[7] Kosower's Z values,[8,9] Dimroth's E_T values,[10,11] and the π^* scale.[12-19] Among them, the greatest recent attention seems to be focused on the π^* scale, since the π^* values have already been given for the most solvents and are frequently used.

The π^* scale proposed by Kamlet, Abboud, and Taft[12] has been theoretically examined in terms of reaction field theory.[14,20,21] The π^* scale is based on the average observed solvatochromic shifts of the $\pi\pi^*$ electronic transitions in highly polarized aromatic molecules such as *N*,*N*-diethyl-4-nitroaniline, 1-ethyl-4-nitrobenzene and 4-nitroaniline. These molecules have large ground-state dipole moments, and thus have much greater dipole moments in their excited states; nitrobenzene[22] and 4-nitroaniline[23,24] have experimentally confirmed this facts. Accordingly, the π^* scale is characterized by being fundamentally defined by the differences between the solvation energies of the ground and excited states of highly polar solute molecules in solvents. These solvation energies may mainly be due to solute dipole-solvent dipole interactions in the case of polar solvents and to solute dipole-solvent induced dipole interactions in the case of nonpolar solvents. This is because solute molecules have large electric dipole moments in both the ground and excited states. Therefore, the π^* values do not correlate with the solvent spectral shifts of solutes having no or small dipole moments. As shown below, there are, actually, no linear relations between the π^* values and the observed electronic transitions of nonpolar and less polarized molecules such as naphthalene, β-carotene, and chlorobenzene.

On the basis of the theoretical background for solvent spectral frequency shifts of organic molecules, therefore, the π^* scale is modified for nonassociating solvents by proposing a new supplementary scale in order to overcome the shortcoming that the π^* scale cannot be applied to nonpolar and less polarized molecules. It is demonstrated that the present modified parameters are better correlated with the observed solvent spectral frequency shifts of organic molecules and with the observed rate constants for organic reactions in various solvents than is the π^* scale.

Theoretical Background

According to previous papers[25,26] concerning the theoretical treatment of solvent effects on the frequency shifts of the electronic absorption spectra, the wave number (σ_{i0}) of a transition from the ground state to the *i*th-excited state of a neutral solute molecule (A) in a solvent (S) is given by

$$\sigma_{i0}(\mathrm{S}) = \sigma^{\circ}_{i0} + \left[\frac{2(p^{s}_{00})^2\{(p^{\mathrm{A}}_{00})^2 - (\boldsymbol{p}^{\mathrm{A}}_{00}\cdot\boldsymbol{p}^{\mathrm{A}}_{ii})\}}{3hc(4\pi\varepsilon_0)^2kT} + \frac{(p^{s}_{00})^2(\alpha^{\mathrm{A}}_{00}-\alpha^{\mathrm{A}}_{ii})}{hc(4\pi\varepsilon_0)} + \frac{\alpha^{s}_{00}\{(p^{\mathrm{A}}_{00})^2-(p^{\mathrm{A}}_{ii})^2\}}{hc(4\pi\varepsilon_0)} + \frac{3I^{s}_0\alpha^{s}_{00}}{2hc(4\pi\varepsilon_0)} \times \left(\frac{\alpha^{\mathrm{A}}_{00}}{1+I^{s}_0/I^{\mathrm{A}}_0} - \frac{\alpha^{\mathrm{A}}_{ii}}{1+I^{s}_0/I^{\mathrm{A}}_0} \right) \right] \sum_{s=1}^{N} \frac{1}{R^6_{\mathrm{A}s}}. \tag{1}$$

Here, c is the speed of light in vacuum, h Planck's constant, k Boltzmann's constant, ε_0 the permittivity of a vacuum, and T the thermodynamic temperature. The superscripts/subscripts (A and s) denote the solute and the sth solvent molecule, respectively. The corresponding transition energy (in cm^{-1}) of the solute molecule in the vapor state is denoted by σ°_{i0}. The symbols p_{00}, α_{00} and I_0 denote the electric dipole moment, the electric isotropic polarizability and the ionization potential, respectively, for the ground state. The *i*th-excited state values, corresponding to p_{00} and α_{00}, are p_{ii} and α_{ii}, respectively. Moreover, N is the number of solvent molecules and $R_{\mathrm{A}s}$ the distance from A to s. In Eq. 1 the average transition energies for all transitions from both the ground state and the *i*th-excited state to all other states are replaced by I_0, as was done in Ref. 26.

In order to separate the solute and solvent terms in each term of Eq. 1, the following two approximations are made:

$$\sum_{s=1}^{N}\frac{1}{R_{\mathrm{A}s}^{6}}=\frac{4\pi L}{3}\times\frac{d^{s}}{M^{s}}\times\frac{1}{r_{\mathrm{A}}^{3}} \tag{2}$$

and

$$1+\frac{I_0^{s}}{I_0^{\mathrm{A}}}\approx 2. \tag{3}$$

Equation 2 was given by Amos and Burrows.[27] Here, L is the Avogadro constant, M^s and d^s are the relative molecular mass and density, respectively, of the nonassociating solvent, and r_{A} is the radius of a spherical solute molecule. Moreover, the following approximation is made in order to reduce the terms of Eq. 1:

$$p_{00}^{\mathrm{A}}\cdot p_{ii}^{\mathrm{A}}=(p_{ii}^{\mathrm{A}})^2. \tag{4}$$

As pointed out in Ref. 25, the approximation of Eq. 4 leads to a neglect of the Franck-Condon principle.

From the above approximations of Eqs. 2—4, one can write Eq. 1 as

$$\sigma_{i0}(\mathrm{S})=\sigma_{i0}^{\circ}+F_1(\mathrm{S})\times\frac{(p_{00}^{\mathrm{A}})^2-(p_{ii}^{\mathrm{A}})^2}{r_{\mathrm{A}}^{3}}+F_2(\mathrm{S})\times\frac{\alpha_{00}^{\mathrm{A}}-\alpha_{ii}^{\mathrm{A}}}{r_{\mathrm{A}}^{3}}, \tag{5}$$

where

$$F_1(\mathrm{S})=\frac{4\pi L}{3hc}\times\frac{d^{s}}{M^{s}}\times\left\{\frac{2(p_{00}^{s})^2}{3(4\pi\varepsilon_0)^2}+\frac{\alpha_{00}^{s}}{(4\pi\varepsilon_0)}\right\}, \tag{6}$$

and

$$F_2(\mathrm{S})=\frac{4\pi L}{3hc(4\pi\varepsilon_0)}\times\frac{d^{s}}{M^{s}}\times\left\{(p_{00}^{s})^2+\frac{3I_0^{s}\alpha_{00}^{s}}{4}\right\}. \tag{7}$$

From Eqs. 6 and 7, $F_1(\mathrm{S})$ and $F_2(\mathrm{S})$ are obviously related only to a nonassiciating solvent, S. An attempt is made to estimate the empirical relative values for $F_1(\mathrm{S})$ and $F_2(\mathrm{S})$ in the following section.

New Solvent Polarity Parameters

The π_1^* Scale. Instead of the usual π^* scale, the $\pi_1^*(\mathrm{N})$ scale,[28] which is a π^* scale determined from the result of Nicolet and Laurence[29,30] only on *N,N*-dimethyl-4-nitroaniline, is used in this paper, for consistency, since their result is also used for the modified π^* scale of π_1^*. Here, consider the case that in Eq. 5 the contribution of $\{(p_{00}^{\mathrm{A}})^2-(p_{ii}^{\mathrm{A}})^2\}$ to $\sigma_{i0}(\mathrm{S})$ is extremely larger than that of $(\alpha_{00}^{\mathrm{A}}-\alpha_{ii}^{\mathrm{A}})$ is. In this case the term containing $(\alpha_{00}^{\mathrm{A}}-\alpha_{ii}^{\mathrm{A}})$ in Eq. 5 may be assumed to be constant for various solvents. From the above assumption, by taking cyclohexane as the standard solvent, one can write the following equations for the solvents of the Sth solvent and dimethyl sulfoxide (DMSO) according to Eq. 5:

$$\sigma_{i0}(\mathrm{S})-\sigma_{i0}(\text{cyclohexane})\approx\{F_1(\mathrm{S})-F_1(\text{cyclohexane})\}\times\frac{(p_{00}^{\mathrm{A}})^2-(p_{ii}^{\mathrm{A}})^2}{r_{\mathrm{A}}^{3}} \tag{8}$$

and

$$\sigma_{i0}(\mathrm{DMSO})-\sigma_{i0}(\text{cyclohexane})\approx\{F_1(\mathrm{DMSO})-F_1(\text{cyclohexane})\}\times\frac{(p_{00}^{\mathrm{A}})^2-(p_{ii}^{\mathrm{A}})^2}{r_{\mathrm{A}}^{3}}. \tag{9}$$

From Eqs. 8 and 9, we can define $\pi_1^*(\mathrm{N})$ as

$$\pi_1^*(\mathrm{N})=\frac{\sigma_{i0}(\mathrm{S})-\sigma_{i0}(\text{cyclohexane})}{\sigma_{i0}(\mathrm{DMSO})-\sigma_{i0}(\text{cyclohexane})}=\frac{F_1(\mathrm{S})-F_1(\text{cyclohexane})}{F_1(\mathrm{DMSO})-F_1(\text{cyclohexane})}. \tag{10}$$

The $\pi_1^*(\mathrm{N})$ value defined by Eq. 10 is the empirical $\pi_1^*(\mathrm{N})$ scale of Taft et al.[28] for the Sth solvent. According to Eq. 10, the $\pi_1^*(\mathrm{N})$ values for the solvents of cyclohexane and DMSO are obviously 0 and 1, respectively.

From Eq. 10, one obtains

$$F_1(\mathrm{S})=F_1(\text{cyclohexane})+\pi_1^*(\mathrm{N})\times\{F_1(\mathrm{DMSO})-F_1(\text{cyclohexane})\}. \tag{11}$$

On the other hand, when the term containing $(\alpha_{00}^{\mathrm{A}}-\alpha_{ii}^{\mathrm{A}})$ can be neglected compared with the term containing $\{(p_{00}^{\mathrm{A}})^2-(p_{ii}^{\mathrm{A}})^2\}$ in Eq. 5, we can write the following equations for the Sth solvent and the cyclohexane solvent according to Eq. 5:

$$\sigma_{i0}(\mathrm{S})\approx\sigma_{i0}^{\circ}+F_1(\mathrm{S})\times\frac{(p_{00}^{\mathrm{A}})^2-(p_{ii}^{\mathrm{A}})^2}{r_{\mathrm{A}}^{3}} \tag{12}$$

and

$$\sigma_{i0}(\text{cyclohexane})\approx\sigma_{i0}^{\circ}+F_1(\text{cyclohexane})\times\frac{(p_{00}^{\mathrm{A}})^2-(p_{ii}^{\mathrm{A}})^2}{r_{\mathrm{A}}^{3}}. \tag{13}$$

From Eqs. 12 and 13, we define the π_1^* parameter for for the Sth solvent as

$$\pi_1^*=\frac{\sigma_{i0}(\mathrm{S})-\sigma_{i0}^{\circ}}{\sigma_{i0}(\text{cyclohexane})-\sigma_{i0}^{\circ}}=\frac{F_1(\mathrm{S})}{F_1(\text{cyclohexane})}. \tag{14}$$

Obviously, Eq. 14 gives the π_1^* value of 1 for the cyclohexane solvent.

From Eq. 14, we obtain

$$F_1(\mathrm{S})=\pi_1^*\times F_1(\text{cyclohexane}) \tag{15}$$

As mentioned above, for consistency, the π_1^* values are determined by Eq. 14 from the result of Nicolet et al.[29,30] only on *N,N*-dimethyl-4-nitroaniline, as listed in Table 1, since the highly polarized *N,N*-dimethyl-4-nitroaniline molecule may be suited for the determination of the π_1^* scale. The σ_{i0}° value[29] of 31340 cm^{-1} for *N,N*-dimethyl-4-nitroaniline was used.

When the term containing $(\alpha_{00}^{\mathrm{A}}-\alpha_{ii}^{\mathrm{A}})$ can be neglected in Eq. 5, we can also write Eq. 10. By equating Eq. 11 to Eq. 15, we obtain the following relation between π_1^* and $\pi_1^*(\mathrm{N})$ for the Sth solvent:

$$\pi_1^*=1+\pi_1^*(\mathrm{N})\times\left\{\frac{F_1(\mathrm{DMSO})}{F_1(\text{cyclohexane})}-1\right\}. \tag{16}$$

Actually, the correlation between the π_1^* and $\pi_1^*(\mathrm{N})$

Table 1. Values of π_1^*, π_1^*(N), PP, and AN

No.	Solvent	π_1^*	π_1^*(N)	PP	AN
1	Perfluoro(methylcyclohexane)	0.661	−0.30		
2	Perfluorohexane	0.627	−0.34		
3	Perfluorodecalin	0.712	−0.26		
4	Perfluoro(1-methyldecalin)	0.728	−0.24		
5	2-Methylbutane	0.870	−0.12		
6	Pentane	0.886	−0.10		
7	Tetramethylsilane	0.911	−0.08		
8	Hexane	0.915	−0.08	0.000	0.0
9	Heptane	0.927	−0.06	0.002	
10	Dodecane	1.000	0.00		
11	Cyclohexane	1	0	0.051	
12	*cis*-Decalin	1.101	0.09		
13	Tetrachloromethane	1.272	0.24	0.267	8.6
14	Tetrachloroethylene	1.275	0.25		
15	Hexafluorobenzene	1.354	0.32		
16	Trichloroethylene	1.579	0.52		
17	Carbon disulfide	1.611	0.55	0.385	
18	1,4-Difluorobenzene	1.630	0.57		
19	Fluorobenzene	1.718	0.64	0.534	
20	1,3-Dichlorobenzene	1.737	0.66		
21	Chlorobenzene	1.769	0.69	0.577	
22	1,2-Dichloroethane	1.854	0.77	0.675	16.7
23	Bromobenzene	1.804	0.72	0.586	
24	1,2-Dichlorobenzene	1.842	0.76		
25	Iodobenzene	1.864	0.78		
26	Diiodomethane	2.127	1.01		
27	Chloroform	1.813	0.73	0.625	23.1
28	Dichloromethane	1.854	0.77	0.658	20.4
29	Tribromomethane	1.937	0.84		
30	Benzene	1.658	0.59	0.459	8.2
31	Toluene	1.544	0.49	0.423	
32	*p*-Xylene	1.456	0.41	0.377	
33	Mesitylene	1.421	0.38	0.342	
34	Prehnitene	1.468	0.42		
35	1-Chlorobutane	1.494	0.44		
36	1-Bromobutane	1.576	0.52		
37	Iodobutane	1.639	0.57		
38	Dimethyl disulfide	1.810	0.73		
39	Diethyl disulfide	1.718	0.64		
40	Methyl phenyl sulfide	1.870	0.78		
41	Dimethyl sulfide	1.668	0.60		
42	Trimethylene sulfide	1.794	0.71		
43	Pentamethylene sulfide	1.706	0.63		
44	Diethyl sulfide	1.525	0.47		
45	Dibutyl sulfide	1.408	0.37		
46	Tetrahydrothiophene	1.756	0.68		
47	Diisopropyl sulfide	1.421	0.38		
48	Anisole	1.807	0.72	0.587	
49	Bis(2-chloroethyl) ether	1.889	0.80		
50	Dioxolane	1.782	0.70		
51	1,4-Dioxane	1.630	0.56	0.500	10.8
52	Dibenzyl ether	1.845	0.76		
53	Diethyl ether	1.339	0.30	0.264	3.9
54	Dibutyl ether	1.263	0.24	0.213	
55	Tetrahydrofuran	1.699	0.63	0.508	8.0
56	2,2,5,5-Tetramethyltetrahydrofuran	1.358	0.32		
57	Chloroacetonitrile	2.117	1.00		
58	Benzonitrile	1.934	0.84	0.734	15.5
59	Acetonitrile	1.867	0.78	0.720	18.9
60	Dimethylcyanamide	1.915	0.82		
61	Diethyl carbonate	1.516	0.46		
62	Methyl acetate	1.668	0.60	0.477	
63	Ethyl acetate	1.623	0.56	0.484	
64	2-Butanone	1.778	0.70	0.609	
65	Acetophenone	1.930	0.84		
66	Acetone	1.794	0.71	0.635	12.5
67	Cyclohexanone	1.829	0.74	0.611	
68	*N*,*N*-Dimethylformamide	1.972	0.87	0.760	16.0
69	Tetramethylurea	1.889	0.80		
70	*N*,*N*-Dimethylacetamide	1.949	0.85	0.757	13.6
71	*N*-Methylpyrrolidinone	2.000	0.90		
72	Dimethyl sulfate	1.889	0.80		
73	Diethyl sulfite	1.788	0.71		
74	Dimethyl sulfoxide	2.114	1	0.862	19.3
75	Tetrahydrofuran *S*-oxide	2.117	1.00		
76	Diethyl phosphorochloridate	1.823	0.74		
77	Trimethyl phosphate	1.902	0.81		
78	Triethyl phosphate	1.835	0.75		
79	Hexamethylphosphoric triamide	1.946	0.85	0.765	10.6
80	Pentafluoropyridine	1.585	0.53		
81	2,6-Difluoropyridine	1.873	0.78		
82	2-Fluoropyridine	1.918	0.82		
83	2-Bromopyridine	2.035	0.93		
84	Pyrimidine	1.978	0.88		
85	3-Bromopyridine	1.908	0.82		
86	Pyridine	1.934	0.84	0.707	14.2
87	Quinoline	2.057	0.95		
88	4-Methylpyridine	1.892	0.80		
89	3,4-Dimethylpyridine	1.883	0.79		
90	2,4,6-Trimethylpyridine	1.747	0.67		
91	*N*,*N*,*N*′,*N*′-Tetramethylguanidine	1.835	0.75		
92	*N*,*N*-Dimethylbenzylamine	1.481	0.43		
93	*N*,*N*-Dimethylpiperazine	1.373	0.34		
94	Triethylamine	1.196	0.18	0.111	
95	Tributylamine	1.133	0.12		
96	*N*,*N*-Dimethylcyclohexylamine	1.310	0.28		

values for the 96 solvents listed in Table 1 is given by

$$\pi_1^* = 1.000 + 1.114\times\pi_1^*(\mathrm{N}) \quad (r=1.000). \tag{17}$$

In this paper the correlation coefficient is denoted by r. The exact realization of Eq. 16 means that the π_1^* parameter reflects the same interactions between the solute and solvent as does the π_1^*(N) parameter, i.e., the π_1^* scale is a modified scale of the π_1^*(N) scale. From Eqs. 16 and 17, we obtain the relation $F_1(\mathrm{DMSO})/F_1(\mathrm{cyclohexane})=2.114$. The π_1^* scale is superior to the π_1^*(N) one, as described below.

The π_2^* Scale. In the case of a nonpolar solute molecule, we obtain according to Eq. 5

$$\sigma_{i0}(\mathrm{S}) = \sigma_{i0}^{\circ} + F_2(\mathrm{S})\times\frac{\alpha_{00}^{\mathrm{A}}-\alpha_{ii}^{\mathrm{A}}}{r_{\mathrm{A}}^3}. \tag{18}$$

In this case, by taking the cyclohexane solvent as the standard, the π_2^* parameter can be defined for the Sth solvent as

Table 2. Values of σ_{i0} and π_2^*

No.	Solvent	σ_{i0} / cm^{-1}	π_2^*
(a) From spectral data[a] of naphthalene			
1	Pentane	32198	0.872
2	Hexane	32168	0.973
3	Heptane	32169	0.970
4	Cyclohexane	32160	1
5	2-Methylbutane	32198	0.872
6	2,2-Dimethylbutane	32195	0.882
7	2,3-Dimethylbutane	32181	0.929
8	2-Methylpentane	32187	0.909
9	3-Methylpentane	32181	0.929
10	2,2,4-Trimethylpentane	32179	0.936
11	2,2,5-Trimethylhexane	32161	0.997
12	Methylcyclopentane	32171	0.963
13	Cyclopentane	32160	1.000
14	Methylcyclohexane	32154	1.020
15	Undecane	32139	1.071
16	Tridecane	32127	1.111
17	2-Chloropropane	32166	0.980
18	2-Chlorobutane	32156	1.014
19	1-Chloropropane	32164	0.986
20	1-Chlorobutane	32140	1.068
21	2-Chloropentane	32153	1.024
22	1-Chloropentane	32133	1.091
23	1-Chloroheptane	32136	1.081
24	1,1,1-Trichloroethane	32118	1.142
25	1,2-Dichloropropane	32127	1.111
26	1,3-Dichloropropane	32127	1.111
27	Dichloromethane	32114	1.155
28	1-Chlorodecane	32127	1.111
29	1,2-Dichloroethane	32123	1.125
30	*cis*-Dichloroethylene	32108	1.176
31	*trans*-Dichloroethylene	32115	1.152
32	Chloroform	32090	1.236
33	1,2,3-Trichloropropane	32102	1.196
34	Trichloroethylene	32073	1.294
35	1,1,2,2-Tetrachloroethane	32080	1.270
36	Tetrachloroethylene	32044	1.392
37	1,5-Cyclooctadiene	32092[b]	1.230
38	1,2-Dibromoethane	32031[b]	1.436
39	1-Bromobutane	32120[b]	1.135
40	1,4-Dioxane	32144[b]	1.054
41	Diethyl ether	32220[c]	0.797
42	Acetonitrile	32190[c]	0.899
(b) From spectral data[d] of β-carotene			
43	Ethyl acetate	22046	1.010
44	Nonane	22070	0.999
45	Dodecane	21988	1.037
46	*N*,*N*-Dimethylformamide	21622	1.208
47	Hexadecane	21905	1.076
48	Tetrachloromethane	21630	1.204
49	Decalin	21788	1.131
50	Benzene	21575	1.230
51	Pyridine	21346	1.337
52	Cyclohexylbenzene	21488	1.270
53	Tetralin	21434	1.296
54	Ethyl cinnamate	21298	1.359
55	Iodobenzene	20999	1.498
56	Carbon disulfide	20730	1.624
(c) From spectral data[b] of anthracene			
57	Tetradecane	26564	1.029
58	Acetone	26579	1.010
59	2-Pentanone	26568	1.024
60	3-Pentanone	26548	1.050
61	2-Heptanone	26509	1.100
62	3-Heptanone	26518	1.089
63	2-Octanone	26511	1.098
64	Acetophenone	26272	1.407
65	Bromobenzene	26272	1.407
66	1-Bromonaphthalene	26109	1.617
67	Benzonitrile	26278	1.399
68	Propionaldehyde	26536	1.066
69	Butyraldehyde	26518	1.089
70	Nitromethane	26483	1.134
71	Nitroethane	26501	1.111
72	1-Nitropropane	26501	1.111

a) Ref. 31. b) Ref. 32. c) Ref. 33. d) Ref. 35.

$$\pi_2^* = \frac{\sigma_{i0}(\mathrm{S}) - \sigma_{i0}^{\circ}}{\sigma_{i0}(\mathrm{cyclohexane}) - \sigma_{i0}^{\circ}} = \frac{F_2(\mathrm{S})}{F_2(\mathrm{cyclohexane})}. \tag{19}$$

From Eq. 19, of course, the π_2^* value for cyclohexane is unity.

From Eq. 19,

$$F_2(\mathrm{S}) = \pi_2^* \times F_2(\mathrm{cyclohexane}). \tag{20}$$

The data of solvent spectral shifts measured by Weigang et al.[31] for the $^1\mathrm{L}_b$ transition of naphthalene are used for the determination of π_2^* values by Eq. 19, where the σ_{i0}° value for the transition is 32456 cm^{-1}.[31] Moreover, additional data[32,33] must be used, since the data of Weigang et al. are limited. The values estimated for π_2^* are listed in Table 2. Out of the spectral data of Weigang et al., the data points for the solvents of tetrachloromethane and nonane were excluded, because tetrachloromethane forms a charge-transfer complex with benzene[34] and the π_2^* value (1.088) calculated by using the datum for nonane is slightly

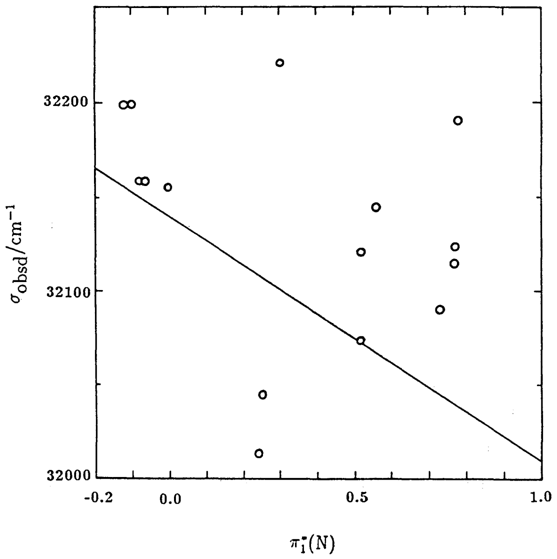

Fig. 1. Correlation of π_1^*(N) with the $^1\mathrm{L}_b$ band of naphthalene.

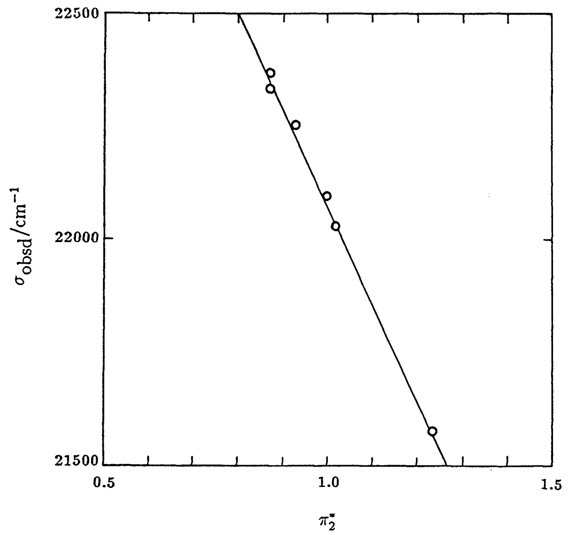

Fig. 2. Correlation of π_2^* with the band of β-carotene.

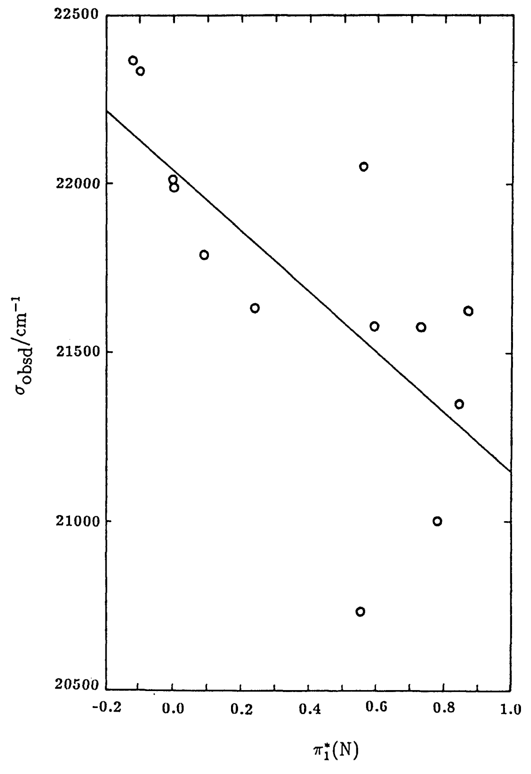

Fig. 3. Correlation of $\pi_1^*(N)$ with the band of β-carotene.

different from that calculated by using the datum for β-carotene. In the case of the nonane solvent, the π_2^* value calculated for β-carotene is alternatively adopted.

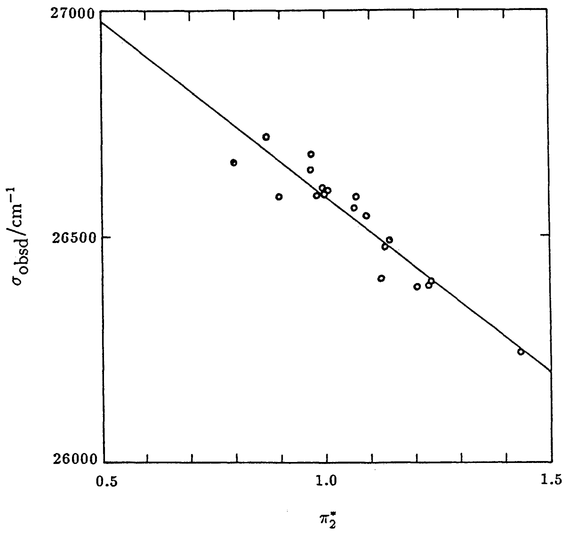

Fig. 4. Correlation of π_2^* with the ^1L_a band of anthracene.

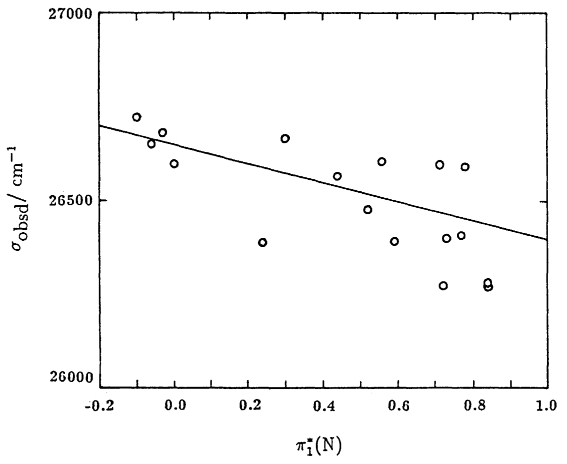

Fig. 5. Correlation of $\pi_1^*(N)$ with the ^1L_a band of anthracene.

As shown in Fig. 1, the correlation between the $\pi_1^*(N)$ values and the 15 solvent spectral shifts for naphthalene is very bad (r=0.322). This is the reason for the necessity of the present proposal of the π_2^* scale for a nonpolar solute, such as naphthalene. As shown in Fig. 2, the correlation of the new π_2^* values with the 6 solvent spectral shift data[35] of β-carotene is excellently given by

$$\sigma_{i0}(S)_{calcd}=24213\ cm^{-1}-2145\ cm^{-1}\times\pi_2^*\quad(r=0.994).\quad(21)$$

Of course, the correlation betwen the $\pi_1^*(N)$ values and the 15 solvent spectral shift data of β-carotene is not good (r=0.706), as shown in Fig. 3. By applying Eq. 21 to the spectral data[35] of β-carotene for solvents whose π_2^* values were unkown, the π_2^* values were calculated, as listed in Table 2.

As shown in Fig. 4, the application of the π_2^* scale to the solvent spectral shifts[32] of the nonpolar anthracene molecule gives the following good correlation:

$$\sigma_{i0}(S)_{calcd}=27361\ cm^{-1}-774.2\ cm^{-1}\times\pi_2^*\quad(r=0.934).\quad(22)$$

The first term of 27361 cm^{-1} corresponds to the σ_{i0}° value, as described below. The observed σ_{i0}° valued[32] of 27590 cm^{-1} agrees well with the above-estimated value. The correlation between the $\pi_1^*(N)$ values and the solvent spectral shifts of anthracene is not good

(r=0.701) as shown in Fig. 5. In order to increase the π_2^* values in number for solvents whose π_2^* were unknown, the π_2^* values were estimated by using Eq. 22 to these solvent spectral shifts of anthracene, as listed in Table 2.

Discussion

In Eq. 1, all interaction modes of the dipole-dipole and dipole-induced dipole interactions and dispersion forces between the solute and solvent molecules are included. According to Eq. 5, the solvent parameter of $F_1(\mathrm{S})$ is related to the solute dipole-solvent dipole interactions and the solute dipole-solvent induced dipole interactions, and $F_2(\mathrm{S})$ is related to the solvent dipole-solute induced dipole interactions and the dispersion forces. Accordingly, the present parameters of π_1^* and π_2^* defined by Eqs. 14 and 19, respectively, have the same above physical meanings that $F_1(\mathrm{S})$ and $F_2(\mathrm{S})$, respectively, have. This is because π_1^* or π_2^* is related only to the values of $F_1(\mathrm{S})$ or $F_2(\mathrm{S})$, according to Eq. 14 or 19. It should be noted that the dispersion forces are not considered in the $\pi_1^*(\mathrm{N})$ parameter as well as the π_1^* parameter, because neither of the parameters are related to $F_2(\mathrm{S})$.

Equation 1 was derived based on the assumptions that a system consists of a neutral solute molecule (A) and N identical neutral solvent molecules and that there are no specific interactions between the solute and solvent molecules. Thus, under the conditions that a neutral solute molecule does not form a hydrogen bond or complex with the neutral solvent molecules in a dilute solution of A, the parameters of π_1^* and π_2^* have the above-mentioned physical meanings.

As described above, the approximation of Eq. 4 leads to a neglect of the Franck-Condon principle.[25] Therefore, Eq. 5 is an approximation derived by neglecting the Franck-Condon principle. Accordingly, the solute terms of $\{(p_{00}^{\mathrm{A}})^2-(p_{ii}^{\mathrm{A}})^2\}/r_{\mathrm{A}}^3$ and $(\alpha_{00}^{\mathrm{A}}-\alpha_{ii}^{\mathrm{A}})/r_{\mathrm{A}}^3$ in Eq. 5 are not suited for estimations of p_{ii}^{A} and α_{ii}^{A} from the solvent spectral frequency shifts.

In a previous paper,[36] $\sum(1/R_{\mathrm{A}s}^6)$ was approximated by

$$\sum_{s=1}^{N}\frac{1}{R_{\mathrm{A}s}^6}=\frac{\pi}{r_s^2}\times\{(r_{\mathrm{A}}+r_s)^{-4}+(r_{\mathrm{A}}+3r_s)^{-4}+(r_{\mathrm{A}}+5r_s)^{-4}\},\quad(23)$$

where r_s is the radius of a spherical solvent molecule. Equation 23 is suited to the present model, but is not appropriate to the present purpose, since Eq. 23 cannot be explicitly divided into two terms each concerning only the solute or solvent. Therefore, $\sum(1/R_{\mathrm{A}s}^6)$ is, for covenience, approximated by Eq. 2. The use of Eq. 2 results in some unfavorable estimations of the values for π_1^* and π_2^*.

In Table 2 there is not a sufficient number of the necessary π_2^* values to apply them. An attempt has, therefore, been made to find a relationship between the π_2^* scale and some property of the solvent in order to estimate an unknown π_2^* value from the property. Among the 42 solvents listed in Table 2, (a), there are 37 solvents whose refractive indexes (n_{D}) at room temperature (mainly at 25 °C) are available. For the 37 solvents, the following empirical correlation was found:

$$\pi_{2,\mathrm{calcd}}^*=-1.137+1.098\times(n_{\mathrm{D}})^2\quad(r=0.957).\qquad(24)$$

For solvents whose π_2^* values are not listed in Table 2, the π_2^* values are, for convenience, estimated from Eq. 24 below.

The present parameter of π_1^* correlated well with the statistical scale of PP proposed by Pytela[5,b] for 33 data points in Table 1:

$$\mathrm{PP}_{\mathrm{calcd}}=-0.707+0.734\times\pi_1^*\quad(r=0.990).\qquad(25)$$

The good correlation means that the PP parameter may be related to the same solute dipole-solvent dipole and solute dipole-solvent induced dipole interactions as is the π_1^* parameter.

Mayer et al.[37] have proposed the acceptor number (AN) parameter (Table 1) from ^{31}P-NMR measurements of triethylphosphine oxide. The AN parameter for the solvents listed Table 1, in which two solvents with α-values of the solvent hydrogen-bond donor acidities[14] higher than 0.1 were excluded, correlated well with the present parameters of π_1^* and π_2^* for 14 data points by

$$\mathrm{AN}_{\mathrm{calcd}}=-17.2+12.4\times\pi_1^*+6.3\times\pi_2^*\quad(r=0.912).\qquad(26)$$

Here, the π_2^* values not listed in Table 2 were calculated by Eq. 24. At the present time the correlation cannot be theoretically explained, because the acceptor number has been determined in a quite different way from the present parameters.

Putting Eqs. 15 and 20 into Eq. 5,

$$\sigma_{i0}(\mathrm{S})=\sigma_{i0}^{\circ}+\pi_1^*\times f_1+\pi_2^*\times f_2,\qquad(27)$$

where

$$f_1=F_1(\text{cyclohexane})\times\frac{(p_{00}^{\mathrm{A}})^2-(p_{ii}^{\mathrm{A}})^2}{r_{\mathrm{A}}^3}\qquad(28)$$

and

$$f_2=F_2(\text{cyclohexane})\times\frac{\alpha_{00}^{\mathrm{A}}-\alpha_{ii}^{\mathrm{A}}}{r_{\mathrm{A}}^3}.\qquad(29)$$

Here, F_1(cyclohexane) and F_2(cyclohexane) are the $F_1(\mathrm{S})$ and $F_2(\mathrm{S})$ values, respectively, for the cyclohexane solvent in Eq. 5. The application of Eq. 27 to the solvent spectral shift data by a least-squares method gives three coefficients of σ_{i0}°, f_1, and f_2 that are constant for a given solute molecule. By using these coefficients, one can obtain values ($\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}}$) calculated for $\sigma_{i0}(\mathrm{S})$ and compare them with the corresponding experimental values. From Eq. 27, it is known that the first term of Eq. 22 is the σ_{i0}° value, as mentioned above.

As described above, the π_1^* scale is related to the

$\pi_1^*(\mathrm{N})$ scale by Eq. 16. Therefore, the $\pi_1^*(\mathrm{N})$ scale is linearly related to $\sigma_{i0}(\mathrm{S})$ by

$$\sigma_{i0}(\mathrm{S}) = \sigma' + f_1' \times \pi_1^*(\mathrm{N}). \tag{30}$$

Here, σ' and f_1' are constant for a given solute molecule. In this case, however, the constant σ' does not correspond to σ_{i0}°.

Since the Franck-Condon principle is ignored in the present theoretical treatment (as described above), the solvation energy (z) of the solute molecule in the ground state can be written from Eq. 27 (according to Ref 25) as

$$z = -\pi_1^* \times F_1(\text{cyclohexane})\, x - \pi_2^* \times F_2(\text{cyclohexane})\, y, \tag{31}$$

where

$$x = \frac{(p_{00}^{\mathrm{A}})^2}{r_{\mathrm{A}}^3} \tag{32}$$

and

$$y = \frac{\alpha_{00}^{\mathrm{A}}}{r_{\mathrm{A}}^3}. \tag{33}$$

Here x and y are parameters characteristic of the solute molecule in the ground state.

By using the present parameters of π_1^* and π_2^*, the solvent effects on the rate constant (k) and activation energy (E_a) for a thermal decomposition of a neutral solute or for a bimolecular reaction between two kinds of neutral solutes can be discussed on the basis of the Arrhenius equation of $\ln k = \ln A - E_a/RT$, where A is the preexponential factor and R is the gas constant. Let us consider, for example, the bimolecular reaction of A+B→products. In the present treatment, the solvent effects on the preexponential factor are assumed to be ignored, as usual.[38] The activation energy for the reaction in the vapor phase is denoted by E_{a}°. An activated complex is indicated by $\mathrm{M}^{\ddagger}$ Then, using Eq. 31, we write the activation energy for the reaction in a solvent as

$$E_{\mathrm{a}} = E_{\mathrm{a}}^{\circ} - z_{\mathrm{A}} - z_{\mathrm{B}} + z_{\mathrm{M}^{\ddagger}} = a + \pi_1^* \times b + \pi_2^* \times d, \tag{34}$$

where

$$a = E_{\mathrm{a}}^{\circ}, \tag{35}$$

$$b = \left\{\frac{(p_{00}^{\mathrm{A}})^2}{r_{\mathrm{A}}^3} + \frac{(p_{00}^{\mathrm{B}})^2}{r_{\mathrm{B}}^3} - \frac{(p_{00}^{\mathrm{M}^{\ddagger}})^2}{r_{\mathrm{M}^{\ddagger}}^3}\right\} \times F_1(\text{cyclohexane}), \tag{36}$$

and

$$d = \left\{\frac{\alpha_{00}^{\mathrm{A}}}{r_{\mathrm{A}}^3} + \frac{\alpha_{00}^{\mathrm{B}}}{r_{\mathrm{B}}^3} - \frac{\alpha_{00}^{\mathrm{M}^{\ddagger}}}{r_{\mathrm{M}^{\ddagger}}^3}\right\} \times F_2(\text{cyclohexane}). \tag{37}$$

Accodingly, $\ln k$ can be written as

$$\ln k = e + \pi_1^* \times f + \pi_2^* \times g, \tag{38}$$

where

$$e = \ln A - \frac{E_{\mathrm{a}}^{\circ}}{RT}, \tag{39}$$

$$f = -\frac{b}{RT}, \tag{40}$$

and

$$g = -\frac{d}{RT}. \tag{41}$$

According to Eqs. 34 and 38, the observed activation energies and logarithmic rate constants, respectively, for a reaction in different solvents can be correlated with the parameters of π_1^* and π_2^* for the solvents. Coefficients a, b, and d in Eq. 34 and those e, f, and g in Eq. 38 can be obtained by least-squares analysis. By using these coefficients, the values for E_{a} and $\ln k$ can be calculated and compared with the corresponding observed values. In the case of a unimolecular reaction, p_{00}^{B} and α_{00}^{B} disappear in Eqs. 36 and 37.

When the $\pi_1^*(\mathrm{N})$ is used instead of π_1^*, the following equations are easily obtained:

$$E_{\mathrm{a}} = a' + b' \times \pi_1^*(\mathrm{N}) \tag{42}$$

and

$$\ln k = e' + f' \times \pi_1^*(\mathrm{N}), \tag{43}$$

because the $\pi_1^*(\mathrm{N})$ scale is related to the π_1^* scale by Eq. 16. Here a', b', e', and f' are constant for a given reaction. In this case, a' is not equal to E_{a}°.

Thus, by using the newly proposed empirical parameters of π_1^* and π_2^*, one can discuss the solvent effects on the rate constants and activation energies for reactions of neutral reactant molecules in various non-associating solvents, as shown in the next section.

Applications

Solvent Spectral Frequency Shifts. In order to stress the necessity of the π_2^* scale, Eq. 27 has been applied to several nonpolar and less polarized solute molecules. In applying Eqs. 27 and 30, only data for solvents whose π_1^* and $\pi_1^*(\mathrm{N})$ values are listed in Table 1 were chosen. The π_2^* values not listed in Table 2 were estimated from Eq. 24.

$\mathbf{C_{30}}$-Polyene: It is shown in Fig. 3 that the solvent spectral frequency shifts of β-carotene do not correlate with the $\pi_1^*(\mathrm{N})$ values. Such a noncorrelation is not restricted to β-carotene of polyenes. For example, the correlations of the solvent spectral shift[39] of the nonpolar $\mathrm{C_{30}}$-polyene molecule with the π_2^* and $\pi_1^*(\mathrm{N})$ values were obtained by applying Eqs. 27 and 30, respectively, to the spectral data for 8 solvents as follows:

$$\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}} = 29070\ \mathrm{cm^{-1}} - 2430\ \mathrm{cm^{-1}} \times \pi_2^* \qquad (r = 0.992)$$

and

$$\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}} = 26490\ \mathrm{cm^{-1}} - 600\ \mathrm{cm^{-1}} \times \pi_1^*(\mathrm{N}) \qquad (r = 0.388).$$

Obviously, the spectral shifts correlate well with the π_2^* values, but do not correlate with the $\pi_1^*(\mathrm{N})$ values.

Fluorene: The solvent effects on the 0-0 band of the $\mathrm{S_0} \rightarrow \mathrm{S_1}$ transition of fluorene have been investigated by Mohler and Wirth.[40] According to them, fluorene is a polar molecule. Data for 8 solvents were chosen out of their reported total of 24 solvents by excluding alcohols and solvents whose π_1^* values were not available in Table 1. The applications of Eqs. 27 and 30 to the chosen data gave the following correlations:

$$\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}} = 16948\ \mathrm{cm}^{-1} + 114\ \mathrm{cm}^{-1} \times \pi_1^* - 439\ \mathrm{cm}^{-1} \times \pi_2^* \quad (r = 0.969)$$

and

$$\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}} = 16651\ \mathrm{cm}^{-1} - 83\ \mathrm{cm}^{-1} \times \pi_1^*(\mathrm{N}) \quad (r = 0.519).$$

The above equations show that the π_1^* and π_2^* values give a good correlation but that the $\pi_1^*(\mathrm{N})$ values do not. In the case of the π_1^* and π_2^* parameters, the $\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}}$ value for the benzene solvent deviated much more from the corresponding $\sigma_{i0}(\mathrm{S})_{\mathrm{obsd}}$ value. This may be due to a π-π association between the aromatic rings of fluorene and benzene.[40]

Chlorobenzene: Macovei[41] have investigated the effects of a solvent on the 0-0 vibrational components[42] of the 37052 cm^{-1} ππ* band of chlorobenzene in the vapor phase. The ground-state dipole moment of chlorobenzene is 1.782 D(1D=3.333X10^{-30} Cm). Data for 14 solvents from his reported data involving 27 solvents were chosen. The results are shown in Fig. 6. Obviously, the spectral shifts correlate with the parameters of π_1^* and π_2^* (r=0.847) but not with the $\pi_1^*(\mathrm{N})$ values (r=0.021). This is probably due to the result that the coefficient (−482 cm^{-1}) of π_2^* is much larger than that (64 cm^{-1}) of π_1^* in the equation for $\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}}$. Moreover, the first term of 37196 cm^{-1} in the equation agrees well with the observed σ_{i0}° value of 37052 cm^{-1}.

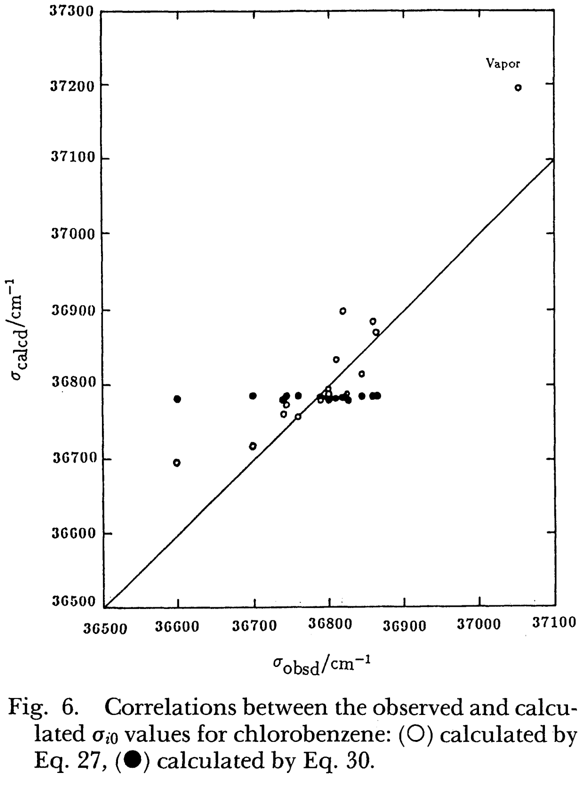

Fig. 6. Correlations between the observed and calculated σ_{i0} values for chlorobenzene: (○) calculated by Eq. 27, (●) calculated by Eq. 30.

Azulene: From spectral data[31] for the $^1\mathrm{L_b}$ and $^1\mathrm{L_a}$ bands of azulene, 7 and 8 data points, respectively, were chosen. The results are given by the following equations:

For the $^1\mathrm{L_b}$ band,

$$\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}} = 14210\ \mathrm{cm}^{-1} + 208\ \mathrm{cm}^{-1} \times \pi_1^* - 83\ \mathrm{cm}^{-1} \times \pi_2^* \quad (r{=}0.967),$$

and

$$\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}} = 14332\ \mathrm{cm}^{-1} + 206\ \mathrm{cm}^{-1} \times \pi_1^*(\mathrm{N}) \quad (r{=}0.952).$$

For the $^1\mathrm{L_a}$ band,

$$\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}} = 29705\ \mathrm{cm}^{-1} + 142\ \mathrm{cm}^{-1} \times \pi_1^* - 514\ \mathrm{cm}^{-1} \times \pi_2^* \quad (r{=}0.933)$$

and

$$\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}} = 29322\ \mathrm{cm}^{-1} + 13\ \mathrm{cm}^{-1} \times \pi_1^*(\mathrm{N}) \quad (r{=}0.059).$$

These results show that the applications of the π_1^* and π_2^* parameters give good correlations for both the $^1\mathrm{L_b}$ and $^1\mathrm{L_a}$ bands and provide good estimations of 14210 and 29705 cm^{-1} for the observed σ_{i0}° values[31] of 14270 and 29760 cm^{-1}, respectively. The $\pi_1^*(\mathrm{N})$ scale does not correlate with the $^1\mathrm{L_a}$ band.

The Neutral 2,2′-Bipyridine Organometallic Complex: The metal-to-ligand charge-transfer transition energies in the neutral 2,2′-bipyridine (bpy) organometallic complex of fac-Re(bpy)(CO)$_3$phen have been reported by Sullivan.[43] From his reported total of 17 data points, 15 data points were chosen. The results are given by the following equations:

$$\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}} = 16590\ \mathrm{cm}^{-1} + 5140\ \mathrm{cm}^{-1} \times \pi_1^* - 2360\ \mathrm{cm}^{-1} \times \pi_2^* \quad (r{=}0.938)$$

and

$$\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}} = 18760\ \mathrm{cm}^{-1} + 5800\ \mathrm{cm}^{-1} \times \pi_1^*(\mathrm{N}) \quad (r{=}0.810).$$

The application of the π_1^* and π_2^* parameters gives slightly better correlations than does the $\pi_1^*(\mathrm{N})$ scale. This small difference in the correlations may be due to the large dipole moment of the organometallic complex.

Acetone: Applications of the π_1^* and π_2^* parameters and the $\pi_1^*(\mathrm{N})$ scale were made to the solvent spectral shifts[44] of acetone. From a total of 13 data points, 11 data points for solvents were chosen. The results are given by the following equations:

$$\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}} = 35700\ \mathrm{cm}^{-1} + 700\ \mathrm{cm}^{-1} \times \pi_1^* - 610\ \mathrm{cm}^{-1} \times \pi_2^* \quad (r{=}0.980)$$

and

$$\sigma_{i0}(\mathrm{S})_{\mathrm{calcd}} = 35820\ \mathrm{cm}^{-1} + 640\ \mathrm{cm}^{-1} \times \pi_1^*(\mathrm{N}) \quad (r{=}0.932).$$

The correlation of the spectral shifts with the π_1^* and π_2^* parameters is slightly better than that with the $\pi_1^*(\mathrm{N})$ scale is. As in the case of the acetone molecule, having a dipole moment of 2.90 D, the correlation of the solvent spectral shifts of a considerably polarized solute molecule with the $\pi_1^*(\mathrm{N})$ scale approches that with the π_1^* and π_2^* parameters.

Rate Constants and Activation Energies. In order to demonstrate the superiority of the presented solvent parameters of π_1^* and π_2^* over the $\pi_1^*(\mathrm{N})$ scale, Eqs. 34, 38, 42, and 43 should be applied to kinetic data for reactions in which only the nonpolar or less polarized neutral chemical species take part. Unfortunately, however, no such reliable kinetic data for the reactions are available, except for only an example of rate constants for the radiative deactivation of a singlet molecular oxygen. Applications of Eqs. 38 to several recent data for the solvent effects on the rate constants of thermal unimolecular and bimolecular reactions of neutral reactants were successfully made; in all these reactions, however, some highly polarized chemical species took part and applications of Eq. 43 for the $\pi_1(\mathrm{N})$ scale to these reactions were similarly successful. A few of the above applications will be described below in order to stress the usefulness of the present solvent parameters of π_1^* and π_2^* which have clear physical meanings. In applying Eqs. 34, 38, 42, and 43, only kinetic data for the nonassociating solvents (whose π_1^* and $\pi_1^*(\mathrm{N})$ values are listed in Table 1) were chosen. The π_2^* values not listed in Table 2 were estimated from Eq. 24. Of course, data for solvents which were capable of forming hydrogen bonds or complexes with solutes were excluded.

Decompositions of *t*-Butyl Halides: Abraham et al.[45] have reported data for the decomposition rates of *t*-butyl halides in various solvents at 25 °C. Out of their total of 21 data points, data points for solvents whose α values of solvent hydrogen-bond donor acidities[14,15] were above 0.2, were excluded, because their analyses (based on empirical solvent parameters) show that the contribution of the α value to $\log k$ is great. The applications of 9 data points from the total of 21 data points for each *t*-butyl halide gave the following equations:

For *t*-butyl chloride,

$$(\log(k/s^{-1}))_{\mathrm{calcd}} = -20.91 + 7.94 \times \pi_1^* - 3.07 \times \pi_2^* \qquad (r=0.974)$$

and

$$(\log(k/s^{-1}))_{\mathrm{calcd}} = -15.02 + 7.10 \times \pi_1^*(\mathrm{N}) \qquad (r=0.955).$$

For *t*-butyl bromide,

$$(\log(k/s^{-1}))_{\mathrm{calcd}} = -18.95 + 8.54 \times \pi_1^* - 3.39 \times \pi_2^* \qquad (r=0.980)$$

and

$$(\log(k/s^{-1}))_{\mathrm{calcd}} = -12.62 + 7.61 \times \pi_1^*(\mathrm{N}) \qquad (r=0.961).$$

For *t*-butyl iodide,

$$(\log(k/s^{-1}))_{\mathrm{calcd}} = -16.34 + 8.31 \times \pi_1^* - 3.92 \times \pi_2^* \qquad (r=0.975)$$

and

$$(\log(k/s^{-1}))_{\mathrm{calcd}} = -10.59 + 7.03 \times \pi_1^*(\mathrm{N}) \qquad (r=0.946).$$

The good correlations of log *k* with the π_1^* and π_2^* parameters are slightly better than the corresponding ones with $\pi_1^*(\mathrm{N})$ scale are. According to Eq. 36, in which p_{00}^{B} disappears in this case, the positive *f* value for each *t*-butyl halide in Eq. 38 means that the dipole moment of each activated complex is much larger than that of the corresponding *t*-butyl halide, because $r_{\mathrm{A}} \approx r_{\mathrm{M}^\ddagger}$ in this case. This result agrees with that of Abraham et al.[45]

Table 3. Comparison of Calculated and Experimental Values for $(\log A - E_a^\circ/2.303RT)$ at 25 °C

t-Butyl halide	Calcd	Exptl[a)]
t-Butyl chloride	−20.91	−19.25
t-Butyl bromide	−18.95	−16.76
t-Butyl iodide	−16.34	−14.30

a) Values calculated from experimental data.[46]

According to Eq. 39, the *e* values in the above equations concerning the π_1^* and π_2^* parameters for $(\log k)_{\mathrm{calcd}}$ are the estimated values for $(\log A - E_a^\circ/2.303RT)$, as shown in Table 3. The average observed values of $\log A$ and E_a° for the decompositions of the *t*-butyl halides in the gas phase have been reported.[46] By using these observed values, experimental values for $(\log A - E_a^\circ/2.303RT)$ were obtained, as listed in Table 3. Table 3 shows that the values calculated for $(\log A - E_a^\circ/2.303RT)$ at 25 °C approximately agree with the corresponding experimental values. Such a dicussion cannot be made from the above equations concerning the $\pi_1^*(\mathrm{N})$ scale.

Abraham and Abraham[47] reported various solvent effects on the activation energies for the decomposition of *t*-butyl chloride. From their reported total of 7 data points, only 4 data points for the solvents of heptane, acetone, acetonitrile, and *N,N*-dimethylformamide were chosen. Applications of Eqs. 34 and 42 to the 4 data points gave the following equations:

$$E_{\mathrm{a,calcd}} = 50.8\ \mathrm{kcal\,mol^{-1}} - 14.4\ \mathrm{kcal\,mol^{-1}} \times \pi_1^* + 2.5\ \mathrm{kcal\,mol^{-1}} \times \pi_2^* \qquad (r=0.998)$$

and

$$E_{\mathrm{a,calcd}} = 38.9\ \mathrm{kcal\,mol^{-1}} - 15.9\ \mathrm{kcal\,mol^{-1}} \times \pi_1^*(\mathrm{N}) \qquad (r=0.997).$$

Here, 1 $\mathrm{cal_{th}}$=4.184 J. According to Eq. 35, 50.8 kcal mol^{-1} in the above equation concerning the π_1^* and π_2^* parameters is equal to E_a°, whose observed value[47] is 45.0 kcal mol^{-1}. Thus, the present value estimated for E_a° roughly agrees with the observed one.

Reaction of *p*-(Dimethylamino)benzenethiyl Radical: Ito and Matsuda[48] have investigated the solvent effects on the rate constants for the foward reaction of *p*-(dimethylamino)benzenethiyl radical with α-methylstyrene at 23 °C. From their total of 25 data points, 20 were chosen. The results of applications are given by the following good correlations:

$$(\log(k/\mathrm{mol^{-1}\,dm^3\,s^{-1}}))_{\mathrm{calcd}}=5.96-1.51\times\pi_1^*+0.64\times\pi_2^* \quad (r=0.973)$$

and

$$(\log(k/\mathrm{mol^{-1}\,dm^3\,s^{-1}}))_{\mathrm{calcd}}=5.15-1.55\times\pi_1^*(\mathrm{N}) \quad (r=0.934).$$

The correlation of the kinetic data with the π_1^* and π_2^* parameters is slightly better than that with the $\pi_1^*(\mathrm{N})$ scale. Ito and Matsuda[48] also showed that the values for the logarithmic rate constant correlate well with the Kirkwood parameter. As mentioned by them, these good correlations are probably due to a large dipole moment of the radical.

The result that the absolute value of the coefficient (−1.51) of π_1^* is larger than that (0.64) of π_2^* in the above equation means that the dipole-dipole and dipole-induced dipole interactions of the reactants and activated complex with solvent molecules are important. According to Eq. 40, the negative coefficient of π_1^* means that the contribution of the dipole moment of the activated complex is smaller than those of the dipole moments of the reactants. This result is in agreement with that of Ito and Matsuda.[48]

The Menschutkin Reaction of Triethylamine with Ethyl Iodide: Abraham and Grellier[49] reported data of solvent effects on the Menschutkin reaction of triethylamine and ethyl iodide at 25 °C. In the reaction, the uncharged reactants proceed to polar products. From their reported total of 32 data points, 21 for solvents were chosen and applied. The results are shown by the following equations:

$$(\log(k/\mathrm{mol^{-1}\,dm^3\,s^{-1}}))_{\mathrm{calcd}}= -11.44+4.22\times\pi_1^*-0.44\times\pi_2^* \quad (r=0.992)$$

and

$$(\log(k/\mathrm{mol^{-1}\,dm^3\,s^{-1}}))_{\mathrm{calcd}}=-7.63+4.53\times\pi_1^*(\mathrm{N}) \quad (r=0.990).$$

Both of the correlations are excellent. According to Eq. 40, the positive value (4.22) for the coefficient of π_1^* means that the contribution of a dipole moment of an activated complex is much greater than those of the reactants. This result agrees with that of Abraham and Grellier.[49] In the present theoretical background, no ionic interactions are considered at all in defining the π_1^* and π_2^* parameters by Eqs. 14 and 19, respectively. The same statement is true for the $\pi_1^*(\mathrm{N})$ scale. In the present case, both of the reactants are uncharged. Accordingly, the above excellent correlations lead to the suggestion that the activated complex may be uncharged, since a number of investigators have suggested so.[49]

The Radiative Deactivation of Singlet Molecular Oxygen: Scurlock and Ogilby[50] have reported data regarding the solvent effects on the relative rate constant (k_r) for the radiative deactivation (${}^1\Delta_gO_2\rightarrow{}^3\Sigma_g^-O_2$) of the singlet molecular oxygen ${}^1\Delta_gO_2$ at 20°. The transition of the nonpolar molecule ${}^1\Delta_gO_2$ to the nonpolar molecule ${}^3\Sigma_g^-O_2$ should occur through a nonpolar species. From their reported total of 15 data points, 12 for the solvents listed in Table 1 could be chosen. The results are shown in Fig. 7. The correlation of the k_r values with the π_1^* and π_2^* parameters is good (r=0.954). Moreover, the coefficient (0.01) of π_1^* was negligibly small compared with that (1.42) of π_2^*. This means that the solvent effects on the k_r value depend almost on the π_2^* values. On the other hand, the $\pi_1^*(\mathrm{N})$ scale obviously does not correlate with the k_r values (r=0.251). This is the reason for the necessity of the new π_2^* scale.

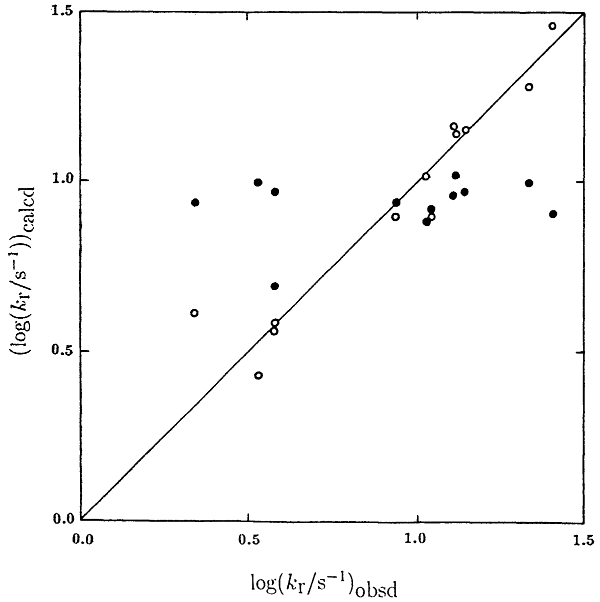

Fig. 7. Correlations between the observed and calculated log k_r values for the radiative deactivation of singlet molecular oxygen in various solvents: (○) calculated by Eq. 38, (●) calculated by Eq. 43.

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References

1) For example, see the book of Ref. 2 and the following recent related papers, Refs. 3, 4, and 5. Almost all references concerning the present problem are cited in Ref. 2.

2) C. Reichardt, "Solvent Effects in Organic Chemisty," 2nd ed, VCH, Weinheim (1988).

3) B. Yu. Zaslavsky, L. M. Miheeva, E. A. Masimov, S. F. Djafarov, and C. Reichardt, *J. Chem. Soc., Faraday Trans.*, **86**, 519 (1990).

4) M. J. Kamlet, R. M. Doherty, M. H. Abraham, Y. Marcus, and R. W. Taft, *J. Phys. Chem.*, **92**, 5244 (1988).

5) a) O. Pytela, *Collect. Czech. Chem. Common.*, **53**, 1333 (1988). b) O. Pytela, *Collect. Czech. Chem. Common.*, **54**, 136 (1989).

6) V. Bekárex, *Collect. Czech. Chem. Common.*, **49**, 2332 (1984).

7) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

8) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

9) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York (1968), pp. 293—304.

10) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Liebigs Ann. Chem.*, **661**, 1 (1963).

11) K. Dimroth and C. Reichardt, *Liebigs Ann. Chem.*, **727**, 93 (1969).

12) M. J. Kamlet, J.-L. M. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 6027, 8325 (1977).

13) J.-L. M. Abboud and R. W. Taft, *J. Phys. Chem.*, **83**, 412 (1979).

14) M. J. Kamlet, J.-L. M. Abboud, and R. W. Taft, *Progr. Phys. Org. Chem.*, **13**, 485 (1981).

15) R. W. Taft, J.-L. M. Abboud, M. J. Hamlet, and M. H. Abraham, *J. Soln. Chem.*, **14**, 153 (1985).

16) R. W. Taft, M. H. Abraham, R. M. Doherty, and M. J. Kamlet, *J. Am. Chem. Soc.*, **107**, 3105 (1985).

17) J.-L. M. Abboud, R. W. Taft, and M. J. Kamlet, *J. Chem. Soc., Perkin Trans. 2,* **1985**, 815.

18) M. J. Kamlet, J.-F. Gal, P.-C. Maria, and R, W. Taft, *J. Chem. Soc., Perkin Trans. 2,* **1985**, 1583.

19) R. M. Doherty, M. H. Abraham, J. M. Harris, R. W. Taft, and M. J. Kamlet, *J. Org. Chem.*, **51**, 4872 (1986).

20) S. Ehrenson, *J. Am Chem. Soc.*, **103**, 6036 (1981).

21) J. E. Brady and P. W. Carr, *J. Phys. Chem.*, **86**, 3053 (1982).

22) H. Labhart and G. Wagniére, *Helv. Chim. Acta*, **44**, 1314 (1963).

23) J. Czekalla and G. Wick, *Z. Elektrochem.*, **65**, 727 (1961).

24) W. Liptay, W. Eberlein, H. Weidenberg, and O. Elflein, *Bunsen-Ges. Phys. Chem.*, **71**, 548 (1967).

25) T. Abe, *Bull. Chem. Soc. Jpn.*, **54**, 327 (1981).

26) a) T. Abe and I. Iweibo, *Bull. Chem. Soc. Jpn.*, **58**, 3415 (1985). b) T. Abe, *Bull. Chem. Soc. Jpn.*, **61**, 3797 (1988).

27) A. T. Amos and B. L. Burrows, *Adv. Quantum Chem.*, **7**, 289 (1973).

28) M. H. Abraham, G. J. Buist, P. L. Grellier, R. A. McGill, D. V. Prior, S. Oliver, E. Turner, J. J. Moris, P. J. Taylor, P. Nicolet, P.-C. Maria, J.-F. Gal, J.-L. M. Abboud, R. M. Doherty, M. J. Kamlet, W. J. Shuely, and R. W. Taft, *J. Phys. Org. Chem.*, **2**, 540 (1989).

29) P. Nicolet and C. Laurence, *J. Chem. Soc., Perkin Trans. 2,* **1986**, 1071.

30) C. Laurence, P. Nicolet, and M. Helbert, *J. Chem. Soc., Perkin Trans. 2,* **1986**, 1081.

31) a) O. E. Weigang, Jr., *J. Chem. Phys.*, **33**, 892 (1960). b) O. E. Weigang, Jr., and D. D. Wild, *J. Chem. Phys.*, **37**, 1180 (1962).

32) M. Nicol, J. Swain, Y.-Y. Shum, R. Merin, and R. H. H. Chen, *J. Chem. Phys.*, **48**, 3587 (1968).

33) T. Abe, Y. Amako, T. Nishioka, and H. Azumi, *Bull. Chem. Soc. Jpn.*, **39**, 845 (1966).

34) C. N. R. Rao, S. N. Bhat, and P. C. Dwivedi, *Appl. Spectrosc. Rev.*, **5**, 1 (1972).

35) A. B. Myers and R. R. Birge, *J. Chem. Phys.*, **73**, 5314 (1980).

36) T. Abe, *Bull. Chem. Soc. Jpn.*, **38**, 1314 (1965).

37) U. Mayer, V. Gutmann, and W. Gerger, *Monatsh. Chem.*, **106**, 1235 (1975).

38) For example, see: E. S. Amis and J. F. Hinton, "Solvent Effects of Chemical Phenomena," Academic Press, New York-London (1973), Vol. 1, Chapter 5.

39) F. Feichtmayr, E. Heilbronner, A. Nürrenback, H. Pommer, and J. Schlag, *Tetrahedron,* **25**, 5383 (1969).

40) C. E. Mohler and M. J. Wirth, *J. Chem. Phys.*, **88**, 7369 (1988).

41) V. Macovei, *Rev. Roum. Chim.*, **21**, 193 (1976).

42) H. Sponor and S. H. Wollam, *J. Chem. Phys.*, **9**, 816 (1941).

43) B. P. Sullivan, *J. Phys. Chem.*, **93**, 24 (1989).

44) W. P. Hayes and C. J. Timmons, *Spectrochim. Acta.* **21**, 529 (1965).

45) M. H. Abraham, R. M. Doherty, M. J. Kamlet, J. M. Harris, and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2,* **1987**, 913.

46) A. Maccoll, *Chem. Rev.*, **69**, 33 (1969).

47) M. H. Abraham and R. J. Abraham, *J. Chem. Soc., Perkin Trans. 2,* **1974**, 47.

48) O. Ito and M. Matsuda, *J. Phys. Chem.*, **88**, 1002 (1984).

49) M. H. Abraham and P. L. Grellier, *J. Chem. Soc., Perkin Trans. 2,* **1976**, 1735.

50) R. D. Scurlock and P. R. Ogilby, *J. Phys. Chem.*, **91**, 4599 (1987).