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Linear Solvation Energy Relationships. 16. Dipole/Dipole Contributions to Formation Constants of Some "Hydrogen Bonded Complexes"

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Formation constants of "hydrogen bonded complexes" of a series of hydrogen bond acceptor (HBA) bases with the hydrogen bond donor (HBD) acids diphenylamine, 4-bromoaniline, and 5-fluoroindole in CCl_4 solvent, chloroform in cyclohexane solvent, and tri-*n*-butylammonium ion in *o*-dichlorobenzene solvent are shown to include important contributions of dipole/dipole interactions. For trifluoroethanol complexes in CCl_4, the dipole/dipole interaction effects are statistically insignificant. Solvent effects on hydrogen bonding and dipole/dipole interactions are analyzed for complexes of 4-fluorophenol with HBA bases.

In previous work on linear solvation energy relationships (LSER's) multiple solvent effects have been unraveled and rationalized in terms of linear combinations of dependences of three indexes of solvent properties (the solvatochromic parameters). The π^* scale is an index of dipolarity/polarizabilities, which measures the ability of the medium to stabilize a dipole or a charge by virtue of its dielectric effect;[1-4] the α scale of hydrogen bond donor (HBD) acidities measures the solvent's ability to donate a proton in a solvent to solute hydrogen bond;[1,5-7] the β scale of hydrogen bond acceptor (HBA) basicities describes the solvent's ability to accept a proton (donate an electron pair) in a solute to solvent hydrogen bond.[1,8-11] The β scale has also been used to evaluate hydrogen bond acceptor strengths of solid HBA bases dissolved in non-HBA solvents.[10]

Among the physicochemical properties and reactivity parameters which contributed to the initial formulation of the β scale[8a] were the formation constants of hydrogen bonded complexes of phenol (**1**) and 4-fluorophenol (**2**) with a series of HBA bases in CCl_4. The log K_f(**1**–HBA) and log K_f(**2**–HBA) values showed excellent linear regressions with β, the correlation coefficients, r, being 0.987 and 0.984, respectively.

In marked contradistinction to the behavior of **1** and **2**, log K_f values of complexes of diphenylamine (**3**) and 4-bromoaniline (**4**) with a number of aliphatic HBA bases in CCl_4 exhibit very poor linear correlation with β. Logarithms of formation constants reported by Lauransan and Pineau[12] are assembled in Table I, together with β and π^* values and dipole moments, μ, of the aliphatic HBA bases. A plot of log K_f(**3**–HBA) vs. β (Figure 1) is virtually a scatter diagram; the correlation coefficient for the least-squares regression equation (represented by the line in the figure) is only 0.46.

Although the r value of 0.87 is considerably higher than that for **3**, the corresponding least-squares correlation of log K_f(**4**–HBA) with β must also be considered as statistically unsatisfactory by the standards which we have applied to linear solvation energy relationships [the better r value for **4** compared with that for **3** is because the latter but not the former data set includes the very much out-of-line data point for triethylamine (μ = 0.7D, π^* = 0.14, β = 0.71)]. Consistent with the above, Lauransan and Pineau observed reasonably good linear correlation of log K_f(**3**–HBA) and log K_f(**4**–HBA) with one another, but poor correlations of either with corresponding log K_f(**1**–HBA) values or with K_f values of HBA base complexes with such other HBD acids as *tert*-butyl alcohol and pyrrole.

We have now found that the measures of goodness of the statistical fits are dramatically better for the linear regression equations of log K_f(**3**–HBA) and log K_f(**4**–HBA) with the dipolarity/polarizability parameter, π^*,[13] and better still if one allows multiple dependences of the K_f's on π^* and β. The correlation equations for **3** are

$$\log K_f(\mathbf{3}\text{–HBA}) = -0.79 + 1.54\pi^* \qquad (1a)$$

$$r = 0.971,\ \sigma \text{ (the standard deviation)} = 0.11$$

$$\log K_f(\mathbf{3}\text{–HBA}) = -1.08 + 1.45\pi^* + 0.60\beta \qquad (1b)$$

$$r = 0.984,\ \sigma = 0.09,\ \mathrm{CL(Ehr)} = 97.5\%$$

and for **4** are

$$\log K_f(\mathbf{4}\text{–HBA}) = -0.98 + 1.55\pi^* \qquad (2a)$$

$$r = 0.973,\ \sigma = 0.10$$

$$\log K_f(\mathbf{4}\text{–HBA}) = -1.17 + 1.23\pi^* + 0.72\beta \qquad (2b)$$

$$r = 0.986,\ \sigma = 0.08,\ \mathrm{CL(Ehr)} = 90\%$$

The CL(Ehr) values given with eq 1b and 2b are the

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(1) Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485.

(2) Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.

(3) Kamlet, M. J.; Hall, T. N.; Boykin, J; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 2599.

(4) Abboud, J. L. M.; Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 8325.

(5) Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1979**, 349.

(6) Taft, R. W.; Kamlet, M. J. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1723.

(7) Taft, R. W.; Kamlet, M. J. *J. Am. Chem. Soc.* **1976**, *98*, 2886.

(8) (a) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377. (b) Yokoyama, T.; Taft, R. W.; Kamlet, M. J. *Ibid.* **1976**, *98*, 3233.

(9) Kamlet, M. J.; Jones, M. E.; Taft, R. W.; Abboud, J. L. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 342.

(10) Kamlet, M. J.; Solomonovici, A.; Taft, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 3734.

(11) We have recently also shown that effects of HBA base solvents on properties of Lewis acid indicators are also linear with β: (a) Taft, R. W.; Pienta, N. J.; Kamlet, M. J; Arnett, E. M. *J. Org. Chem.* **1981**, *46*, 661. (b) Taft, R. W.; Kamlet, M. J. *Org. Magn. Reson.* **1980**, *14*, 485.

(12) Lauransan, J.; Pineau, P. *J. Chim. Phys. Phys.-Chim. Biol.* **1968**, *65*, 1937.

(13) The term *solvent dipolarity* is intended as a more specific description than the often misused *solvent polarity*, which has frequently included as well the effects of hydrogen bonding interactions in varying combinations with the dipole/dipole effects.

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Table I. Formation Constants of Hydrogen Bonded and Dipole/Dipole Complexes

no.[a]	HBA base	π^*	μ, D	β	log K_f[e] 3	4	5	6	7	8
3	triethylamine	0.14	0.7	0.71	−0.431		0.53	−0.43	1.854	
4	diisopropyl ether	0.27	1.2	0.49				−0.52		
5	di-*n*-butyl ether	0.24	1.2	0.46	−0.523	−0.456		−0.61		
7	diethyl ether	0.27	1.2	0.47	−0.301		0.23		0.714	0.964
9	dioxan	0.55	(1.8)[b]	0.37	−0.056	−0.222		−0.59		
11	ethyl acetate	0.55	2.7	0.45				−0.19	0.841	
13	tetrahydrofuran	0.58	1.8	0.55			0.34	−0.29		2.182
18	acetone	0.68	2.9	0.48	0.342			−0.17	0.864	2.398
23	dimethylformamide	0.88	3.8	0.69	0.633	0.398	1.25		1.613	
25	dimethylacetamide	0.88	3.8	0.76			1.47		1.848	4.491
26	hexamethylphosphoramide	0.87	4.7	1.05			2.31	1.05[c]	2.495	6.352
28	*N*-methylpyrrolidone	0.92	4.1	0.77		0.512		0.45		
29	dimethyl sulfoxide	1.00	4.1	0.76	0.851	0.653	1.49		1.851	4.568
41	cyclohexanone	0.76	2.7	0.53	0.255	0.176	0.75	−0.04		
48	tri-*n*-butylamine	0.16	0.7	0.62			0.42	(−1.09)[d]		
51	cyclopentanone	0.76	2.7	0.52	0.322	0.130				
40	tetrahydropyran	0.51	1.8	0.54	−0.125	−0.301		−0.35		

[a] HBA base numbering is the same in all papers of this series. [b] Group dipole (at either end) assumed to be same as for THF or THP. [c] Estimated from a value of 1.190 at 29 °C. [d] Excluded because of strong steric effect. [e] For the following: (3) diphenylamine, CCl_4 solvent, 25 °C;[12] (4) 4-bromoaniline, CCl_4 solvent, 25 °C;[12] (5) 5-fluoroindole, CCl_4 solvent, 25 °C;[16b] (6) chloroform, cyclohexane solvent, 35 °C;[17a] (7) trifluoroethanol, CCl_4 solvent, 24 °C;[18] (8) tri-*n*-butylammonium ion, *o*-dichlorobenzene, solvent, 25 °C.[19]

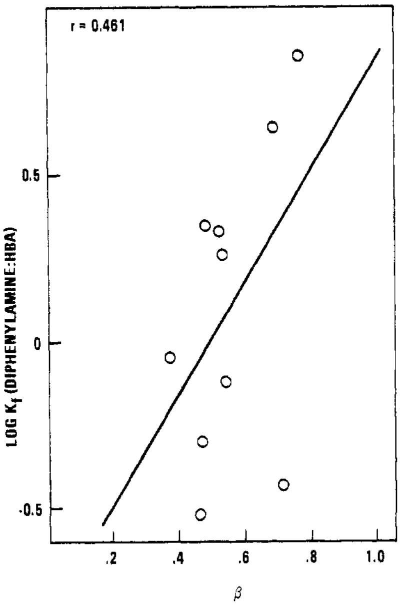

Figure 1. Log K_f(3–HBA) plotted against the HBA basicity parameter β.

confidence limits that the single parameter regressions may be discarded in favor of the dual regressions according to the statistical test set forth by Ehrenson.[14] To warrant inclusion of the additional term, CL(Ehr) should be at least 90%. It is noteworthy that the standard deviations for eq 1b and 2b do not compare unfavorably with the ±15–20% experimental precision (corresponding to 0.06–0.08 log units) claimed by Lauransan and Pineau for the equilibrium constant measurements.

It is necessary to explain why formation constants, determined for the HBA bases acting as solutes in relatively dilute CCl_4 solutions, should correlate with π^* values, which are considered to be dipolarity/polarizability measures[1–4] for the HBA bases acting as bulk solvents. The answer probably lies in the findings, reported earlier by Abboud and co-workers,[4] that the π^* values of most of the aliphatic HBA bases in Table I are very nearly proportional to their molecular dipole moments. It follows, therefore, that the dependences of the log K_f's on the π^* terms in the above equations probably reflect the effects of dipole/dipole interactions between the HBD acids and the HBA bases. Indeed, the correlations in the present paper were restricted to aliphatic HBA bases to specifically exclude variable-polarizability effects of aromatic HBA bases (deriving from dipole/induced dipole interactions).[15]

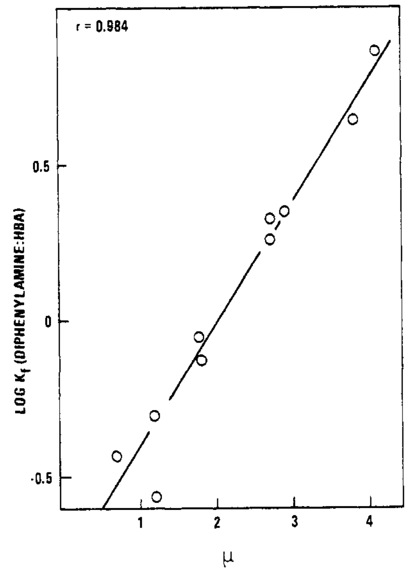

Figure 2. Log K_f(3–HBA) plotted against the dipole moments μ (in D) of the HBA bases.

A logical next step is to eliminate the intermediacy of the π^* terms and correlate the log K_f's directly with the dipole moments, μ, and with linear combinations of μ and β. As is seen in Figure 2, a plot of log K_f for the diphenylamine–HBA complexes against μ shows excellent linearity. The regression equation is shown in eq 3a.

$$\log K_f(3\text{–HBA}) = -0.81 + 0.396\mu \qquad (3a)$$

$$r = 0.984,\ \sigma = 0.09$$

Here, however, the multiple linear regression equation with μ and β shows only a minor improvement in r and, ac-

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(14) Ehrenson, S. *J. Org. Chem.* **1979**, *44*, 1793.

(15) Abboud, J. L. M.; Kamlet, M. J.; Taft, R. W., submitted for publication in *J. Am. Chem. Soc.*

cording to the CL(Ehr) criterion, a statistically insignificant dependence on the HBA basicity parameter (eq 3b). A

$$\log K_f(\text{3-HBA}) = -0.89 + 0.387\mu + 0.177\beta \quad (3b)$$

$$r = 0.985,\ \sigma = 0.09,\ \text{CL(Ehr)} = 50\%$$

somewhat similar situation applies for the log K_f values of the HBA base complexes with 4-bromoaniline. The correlation equation with μ is given in eq 4a, and the

$$\log K_f(\text{4-HBA}) = -0.87 + 0.353\mu \quad (4a)$$

$$r = 0.986,\ \sigma = 0.07$$

multiple linear regression equation with μ and β is, given in eq 4b.

$$\log K_f(\text{4-HBA}) = -0.74 + 0.411\mu - 0.504\beta \quad (4b)$$

$$r = 0.989,\ \sigma = 0.07,\ \text{CL(Ehr)} = 75\%^{16a}$$

Thus, eq 1a–2b and 3a–4b lead to somewhat different conclusions. Both sets of correlations indicate that the dominant dependences of the log K_f values are on the dipole moments, but the CL(Ehr) values for eq 1b and 2b suggest that there is also a smaller, but statistically significant, dependence on the HBA basicities, whereas the Cl(Ehr) values for eq 3b and 4b indicate that the dependences on β are insignificant. Because we believe the experimental precisions of the π^* values to be better than those of the dipole moments (which are from a number of sources and are determined under a variety of conditions), we prefer the former possibility. Either way, however, there seems no question that the dipole/dipole interactions are the main contributors to the free energies of formation of the complexes of diphenylamine and 4-bromoaniline with HBA bases. Lauransan and Pineau's experiences in attempts at intercorrelations between the various log K_f values are completely consistent with these findings.

Nor is the complexation behavior of **3** and **4** unusual. We have found numerous instances of dipole/dipole contributions to formation free energies of hydrogen bonded complexes. For example, Mitsky, Joris, and Taft[16b] had noted earlier that linear correlation was poor when log K_f values for complexes of 5-fluoroindole (**5**) with HBA bases in CCl_4 were plotted against pK_{HB} (pK_{HB} being an earlier HBA basicity measure which is linear with β).[8a] Seemingly better correlations were observed, however, when families of HBA bases with similar acceptor sites (carbonyl and oxide bases, pyridine and guanidine bases, trialkylamine bases) were treated separately. The separation of the log K_f(5–HBA) values into the three family lines was attributed at that time to a steric entropy effect.

We have now confirmed that, even when consideration is limited to aliphatic HBA bases (Table I), the linear correlation of log K_f(5–HBA) values with β is rather poor (eq 5a). Nor is the quality of the linear regression with

$$\log K_f(\text{5-HBA}) = -1.52 + 3.66\beta \quad (5a)$$

$$n = 9,\ r = 0.905,\ \sigma = 0.30$$

μ much better (eq 5b). Here, however, the multiple-parameter least-squares correlation with μ and β leads to a very much better statistical fit, coupled with a very high CL(Ehr) value (eq 5c).

$$\log K_f(\text{5-HBA}) = -0.09 + 0.409\mu \quad (5b)$$

$$r = 0.910,\ \sigma = 0.32$$

$$\log K_f(\text{5-HBA}) = -1.14 + 0.249\mu + 2.14\beta \quad (5c)$$

$$r = 0.994,\ \sigma = 0.08,\ \text{CL(Ehr)} = 99.9\%$$

Equation 5c suggests that the hydrogen bond and the dipole/dipole interaction contribute comparable amounts to the free energies of formation of the 5–HBA complexes. For a representative HBA base like dimethylformamide (μ = 3.8 D, β = 0.76), the ratio of the dipole/dipole term to the hydrogen bonding term is 0.95/1.62. We now prefer such an explanation over the steric entropy effect proposed earlier, and we now consider that the seeming separation into families in the plot of log K_f(5–HBA) against pK_{HB} was an artifact, deriving from the generally lower dipolarity/basicity ratios for the trialkylamine and pyridine bases compared with the oxygen bases.

On the basis of formation constants reported by Takayama, Fujita, and Nakajima,[17a] a similar complexation situation applies for chloroform (**6**) complexes with HBA bases in cyclohexane (Table I). As before, linear correlation of the log K_f values with β is poor[17b] (eq 6a), and the quality of the linear fit with μ is only slightly better (eq 6b). Again the multiple linear regression equation with μ and β shows excellent goodness of fit, coupled with a very high Cl(Ehr) value (eq 6c).

$$\log K_f(\text{6-HBA}) = -1.46 + 2.25\beta \quad (6a)$$

$$n = 11,\ r = 0.868,\ \sigma = 0.26$$

$$\log K_f(\text{6-HBA}) = -1.01 + 0.372\mu \quad (6b)$$

$$r = 0.926,\ \sigma = 0.20$$

$$\log K_f(\text{6-HBA}) = -1.46 + 0.252\mu + 1.23\beta \quad (6c)$$

$$r = 0.995,\ \sigma = 0.07,\ \text{CL(Ehr)} = 99.9\%$$

On comparison of eq 5c and 6c, it is seen that for chloroform complexes in cyclohexane the dipole/dipole interaction term contributes relatively more and the hydrogen bond relatively less than was the case with the 5-fluoroindole complexes in CCl_4. This may, in part, be a solvent effect (as a general rule, the dependences of the log K_f values on μ and β increase with decreasing solvent dipolarity, the effect being greater for the dipole/dipole term; see further discussion below), but it probably also reflects a greater HBD acidity for **5** compared with **6**.

Considering next the somewhat stronger HBD acid, trifluoroethanol (**7**), we encounter a completely different type of situation than was the case with **3**–**6**. Log K_f(7–HBA) values in CCl_4 reported by Sherry and Purcell[18] (Table I) show poor linearity with μ (the r value being only 0.53), but very much better linear regression with β (eq 7a).

$$\log K_f(\text{7-HBA}) = -0.55 + 3.07\beta \quad (7a)$$

$$n = 8,\ r = 0.977,\ \sigma = 0.15$$

Here, however, the multiple linear regression shows an insignificant improvement in the goodness of the statistical fit over eq 7a, as well as a coefficient of μ which is small in magnitude and of the wrong sign (i.e., the dipole/dipole effect seemingly destabilizing the complex):

$$\log K_f(\text{7-HBA}) = -0.54 - 0.036\mu + 3.22\beta \quad (7b)$$

$$r = 0.979,\ \sigma = 0.14,\ \text{CL(Ehr)} = 50\%$$

It is seen that the term in μ is also statistically insignificant

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[16] (a) Note the negative sign of the coefficient of β to which it is difficult to attribute any physical significance. (b) Mitsky, J.; Joris, L.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 3442.

[17] (a) Takamaya, C.; Fujita, T.; Nakajima, M. *J. Org. Chem.* **1979**, *44*, 2871. (b) These workers also observed seemingly separate regression lines against pK_{HB} for different families of HBA bases in a patter of behavior resembling that reported for **5**.[16b] For quite similar reasons, the apparent family behavior was probably an artifact.

[18] Sherry, A. D.; Purcell, K. F. *J. Phys. Chem.* **1970**, *74*, 3535.

Table II. Formation Constants of 4-FC_6H_4OH–HBA Complexes Correlated with β and π^* Values of HBA Bases

solvent	eq	$\log K_0$	b	s	r	SD	n
c-C_6H_{12} ($\pi^* = 0$)	a	−0.776	4.301		0.9925	0.17	5
	b	−0.947	4.109	0.431	0.9991	0.05	5
CCl_4 ($\pi^* = 0.29$)	a	−0.909	4.291		0.984	0.14	19
	b	−1.011	4.096	0.345	0.990	0.11	19
C_6H_5Cl ($\pi^* = 0.71$)	a	−0.773	3.697		0.995	0.10	5
	b	−0.796	3.659	0.075	0.996	0.10	5
o-$C_6H_4Cl_2$ ($\pi^* = 0.80$)	a	−0.964	3.915		0.992	0.13	6
	b	−0.914	3.969	−0.124	0.993	0.12	6
$ClCH_2CH_2Cl$ ($\pi^* = 0.81$)	a	−1.273	3.744		0.977	0.21	6
	b	−1.085	3.964	−0.466	0.990	0.14	6
CH_2Cl_2 ($\pi^* = 0.63$, $\alpha = 0.33$)	a	−1.062	3.401		0.922	0.37	6
	b	−0.654	3.842	−1.017	0.988	0.14	6

[a] $\log K_f$ (2–HBA) = $\log K_0 + b\beta$. [b] $\log K_f$ (2–HBA) = $\log K_0 + b\beta + s\pi^*$.

according to the CL(Ehr) criterion.

Thus, with **3–7**, we have covered the gamut of interaction effects, from predominantly (perhaps exclusively) dipole/dipole for the very weak HBD acids diphenylamine and 4-bromoaniline to blends of hydrogen bond and dipole/dipole effects of comparable magnitudes for the somewhat stronger HBD acids 5-fluoroindole and chloroform to predominantly (perhaps exclusively) hydrogen bond acid/base effects for the still stronger HBD acid trifluoroethanol.

Rather than dipole/dipole interactions, our next example involves contributions of charge/dipole interactions to formation constants of hydrogen bonded complexes. The data (Table I) are those of Gilkerson and co-workers[19] for complexes of tri-n-butylammonium ion (**8**) with HBA bases in o-dichlorobenzene solvent. As is seen in eq 8a and 8b,

$$\log K_f(\mathbf{8}\text{–HBA}) = -0.80 + 1.37\mu \qquad (8a)$$

$$r = 0.963,\ \sigma = 0.60$$

$$\log K_f(\mathbf{8}\text{–HBA}) = -2.31 + 8.55\beta \qquad (8b)$$

$$r = 0.966,\ \sigma = 0.57$$

fair single parameter correlations are obtained between log K_f(**8**–HBA) and both μ and β (the r value for the linear correlation of μ with β for the six HBA bases involved is 0.871). As with **5** and **6**, the goodness of the fit becomes excellent, and a high CL(Ehr) value is obtained for the multiple linear regression equation with μ and β (eq 8c).

$$\log K_f(\mathbf{8}\text{–HBA}) = -1.92 + 0.727\mu + 4.68\beta \qquad (8c)$$

$$r = 0.997,\ \sigma = 0.18,\ \text{CL(Ehr)} = 99.5\%$$

On comparing eq 8c with the earlier correlations, it is seen that, as might be expected, the coefficients of μ and β are greater for the charged than for the uncharged HBD acids. Further, although statistically stronger cases could be made if there were more data for each of the individual correlations, the 52 formation constants in Table I conform with a series of progressions (i.e., with increasing indicator acidity) which comprise a mutually consistant, and hence mutually supporting, framework of linear free energy relationships.

The solvation effects on formation constants were also studied and some thought-provoking results were obtained when we next examined effects of solvent dipolarity on hydrogen bonding and dipole/dipole contributions to formation constants of 4-fluorophenol (**2**) with HBA bases. The data are those of Gurka, Mitsky, Joris, and Taft[16,20] and, as before, are for the aliphatic HBA bases only. The correlations are with β and π^* rather than with β and μ so as to make more readily evident the ratios of the contributions of the dipolarity and the hydrogen bonding effects.[21]

The single- and dual-parameter correlations are summarized in Table II, where it is seen that, while the dominant effects are, indeed, those of the β terms, there are also statistically significant dependences on π^* values of the HBA bases in four of the six solvents. Considering first the b terms in Table II, we see a progression such as might have been anticipated from a priori considerations, i.e., a small and gradual decrease in the magnitude of b with increasing solvent dipolarity, with b remaining always positive in sign.

Completely unanticipated, however, was the behavior of s with increasing solvent dipolarity. It is seen that, as the solvent changes from C_6H_{12} to CCl_4 to chlorobenzene to o-dichlorobenzene to 1,2-dichloroethane to methylene chloride, the initially positive and statistically significant s term decreases in magnitude and becomes statistically insignificant, goes through zero and turns negative, and then increases in magnitude, becoming a highly significant negative contributor to the overall free energy of complex formation in CH_2Cl_2 (in which solvent the negative $s\pi^*$ term offsets ca. 20–30% of the effect of the $b\beta$ term for typical HBA bases).

It remains, then, to explain how increasing dipolarity of the HBA base can destabilize or lessen the formation free energy of the hydrogen bonded complex in the more dipolar solvent. We believe that the answer can be found on examining how the various solute/solute and solute/solvent dipole/dipole interactions affect the equilibrium in eq 9. We consider four types of dipolar interactions:

$$\text{HBA} + \text{HBD} \rightleftarrows \text{HBA–HBD} \qquad (9)$$

(a) the dipolar interaction between HBA and HBD shifts the equilibrium to the right; (b) the dipolar interaction between the complex (whose dipole moment is greater[22] but which is sterically more shielded from the solvent than that of either HBA or HBD) and the solvent also shifts the equilibrium to the right; (c) the dipolar interaction between the solvent and HBD shifts the equilibrium to the left; (d) the dipolar interaction between the solvent and HBA (and the hydrogen bonding interaction in the case of CH_2Cl_2 solvent) also shifts the equilibrium to the left. In the nondipolar or weakly dipolar solvents, interactions c and d are minimal, and interaction a is dominant; the effect of increasing the dipolarity of the HBA base is to

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(19) Aitkin, H. W.; Gilkerson, W. R. *J. Am. Chem. Soc.* **1973**, *95*, 855. Flora, H. B.; Gilkerson, W. R. *Ibid.* **1970**, *92*, 3273. Gilkerson, W. R.; Ezell, J. B. *Ibid.* **1967**, *89*, 808.

(20) Gurka, D.; Taft, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 4794.

(21) Since the π^* and β scales both range from near zero to near 1.0, the b and s terms (the coefficients of β and π^*) are rough relative measures of the dipolarity and hydrogen bonding contributions to formation free energies.

(22) Ratajczak, H. *J. Phys. Chem.* **1972**, *76*, 3000.

shift the equilibrium to the right, thereby stabilizing the hydrogen bonded complex.

In the more dipolar solvents, however, factor c and d become increasingly important, and the phenomenon which destabilizes the hydrogen bonded complex with increasing HBA dipolarity is the dipolar interaction between the HBA base and the solvent, which shifts the equilibrium to the left. Thus, we can rationalize stabilization of the hydrogen bonded complex with decreasing solvent dipolarity and with either increasing or decreasing solute dipolarity.

As a concluding comment, it seems fair to state that certain associated species, previously referred to as hydrogen bonded complexes, might more properly be designated as hydrogen bonded dipolar complexes.

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Unusual Products from the Reactions of Anhydrous Hydrogen Chloride with Arylacetylenes[1]

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Liquid-phase reactions of anhydrous hydrogen chloride with *p*-methyl-, *p*-methoxy-, *p*-fluoro-, and unsubstituted phenylacetylene afforded cyclic trimers, tetramers, and pentamers of the corresponding arylacetylenes. Phenylacetylene gave additionally 1-methyl-1-phenyl-3-chloroindene. The reactions proceeded via the corresponding HCl diadducts, i.e., via 1-aryl-1,1-dichloroethanes as intermediates.

Reactions of monosubstituted acetylenes with hydrogen chloride have been examined under various aspects and a variety of conditions.[2] From the published data it appears that both in the gas phase and in organic solvents the corresponding mono- and/or diadducts are formed. By contrast, reactions of monoalkylacetylenes with anhydrous hydrogen chloride in the liquid phase and in the absence of a solvent provided a greater variety of products. In particular, [2 + 2] cycloadditions to yield the corresponding 1,3-dialkyl-1,3-dichlorocyclobutanes have been observed in all cases examined.[3] To our knowledge, reactions of monosubstituted arylacetylenes under such conditions have not been reported.[4,5] In this paper we describe the results of the reactions of neat hydrogen chloride with phenylacetylene (**1a**) and with *p*-methyl-(**1b**), *p*-methoxy-(**1c**), and *p*-fluorophenylacetylene (**1d**) in the liquid phase and at ambient temperatures.

Reaction Products. Phenylacetylene (1a). Reactions of **1a** with HCl in a molar ratio of 1:5 afforded entirely different products, depending on the reaction time (Scheme I). Termination of the reaction after 1 and after 3 days afforded in each case mobile liquids, whereas after 7 days a highly viscous liquid was obtained, after 13 days a semisolid was obtained, and after 27 days a solid reaction product was obtained. ^{1}H NMR analyses showed that in each case the starting material **1a** had been consumed. Diadduct **4a** was the major reaction product after short reaction times. Its proportion of the total products decreased, however, from 82% (1 day), via 68% (3 days), 20% (7 days), and 11% (13 days) to 6% (27 days). Monoadduct **2a** was also detected by ^{1}H NMR analysis, despite the excess HCl applied. Its proportion was 5% (1 day), 6% (3 days), 2% (7 days), and trace amounts after 13 and 27 days, each. In the ^{1}H NMR spectra of all reaction products, the intensities of the signals in the aromatic region were in excess over those expected for **2a** and **4a**. This excess amounted to 13, 27, 79, 89, and 94% in the products obtained after 1, 3, 7, 13, and 27 days, respectively. This was indicative of the enhanced formation of aromatic products at the expense of diadduct **4a** with increasing reaction times.

GLC analyses of the crude reaction products obtained after 13 and 27 days showed in each case **4a** as the minor component, whereas the major peaks had longer retention times. Chromatographic separation of these products afforded six compounds that corresponded to these peaks. The isolated compounds were assigned to the structures of **15a**–**20a**. From the crude products obtained after 13 days of reaction, the yields of the isolated, purified compounds were 7% for **15a**, 11% for **16a**, 8% for **17a**, 4% for **18a**, and ca. 1% for **19a** and **20a**, each. The actual yields were higher, but the purification resulted in considerable material losses. In addition to compounds **15a**–**20a**, ca. 46 wt % of a dark-brown solid material was isolated. Its ^{1}H NMR spectrum showed predominantly signals in the aromatic region (δ 6.3–8.0) and unstructured, broad signals in the aliphatic region (δ 0.6–2.8). GLC analysis showed no peaks, thus indicating that the material was probably oligomeric or polymeric.

Compounds **15a**–**17a** have been identified with the help of authentic samples: **15a** was prepared by the reaction of phosphorus pentachloride with 3-methyl-3-phenyl-1-

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[1] This paper has been presented by G. Leifker, V. V. Ramana Rao, K. Vittinghoff, and K. Griesbaum, at the 19th Hauptversammlug der Gesellschaft Deutscher Chemiker, held in Hamburg, 1981.

[2] For a summary, see, for example, P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian in "Vinyl Cations", Academic Press, New York, 1979.

[3] G. Stammann and K. Griesbaum, *Chem. Ber.*, **113**, 598 (1980), and references cited therein.

[4] Liquid-phase reactions of anhydrous HCl with the alkylaryl-substituted acetylene-1-phenylpropyne have been carried out in our laboratory. They afforded unusual products, having indene structures. Preliminary results about some reaction products have been reported,[1,5] and a full paper is in preparation.

[5] B. Deppisch and K. Vittinghoff, *Acta. Crystallogr.*, **36**, 3191 (1980).

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