

## A Quantitative Study of Structural Effects on the Self-Association of Alcohols

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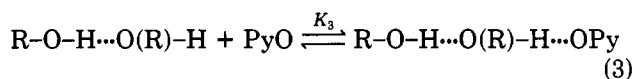
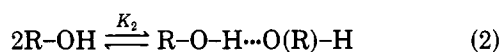
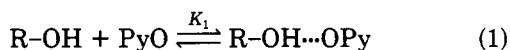
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The constants  $K_1$ ,  $K_2$ , and  $K_3$ , respectively, describing the equilibria  $R-OH + OPy \rightleftharpoons ROH \cdots OPy$ ,  $2ROH \rightleftharpoons (ROH)_2$ , and  $ROH \cdots O(R)-H + OPy \rightleftharpoons R-OH \cdots O(R)-H \cdots OPy$  have been measured at  $20.0 \pm 0.1$  °C in cyclohexane and, in some cases, in carbon tetrachloride, by means of UV spectrometry ( $R = Me, Et, n-Pr, i-Pr, sec-Bu, t-Bu$ , and  $t-Am$ ;  $PyO =$  pyridine  $N$ -oxide). From these results we have determined the relative acidities toward  $PyO$  of these alcohols in their monomeric and dimeric forms. The combination of these data with the available tetramerization constants has allowed the direct quantitative evaluation of the effects of self-association upon the acidity and basicity of monomeric and dimeric alcohols. The fundamental role of steric hindrance in determining the strength and size of alcohols clusters has clearly emerged. These results also show promise in rationalizing the empirical hydrogen-bonding acidity scale  $\alpha$ . This method can be extended to the study of other self-associated hydrogen-bonding acids.

### Introduction and Experimental Results

The quantitative study of pure alcohols has recently received new impetus from very different quarters. Thus, Kamlet, Taft, and their co-workers<sup>3</sup> have developed and extensively used an empirical scale of hydrogen-bonding acidity,  $\alpha$ , which satisfactorily applies to bulk alcohols and other hydrogen-bonding acids. On the other hand, Jorgensen,<sup>4</sup> by means of "ab initio" and Monte-Carlo calculations, has given new insights into the structure of liquid methanol and ethanol, while reproducing a number of their thermodynamic properties. This work provides new experimental data that might be of some interest in the light of these studies. Thus, we have determined the constants  $K_1$ ,  $K_2$ , and  $K_3$  corresponding to the equilibria in eq 1-3



in dilute solution in cyclohexane and, in some cases, carbon tetrachloride at  $20.0 \pm 0.1$  °C ( $PyO =$  pyridine  $N$ -oxide;  $ROH = MeOH, EtOH, n-PrOH, i-PrOH, t-BuOH$ , and  $t-AmOH$ ).

The experimental technique used to determine these constants has been described in detail elsewhere<sup>5</sup> and is summarized in the Appendix. Suffice to say at this point that the method is based upon the fact that the near-UV spectrum of  $PyO$  shows a weak absorption in the 330-350 nm range ( $\lambda_{max}$  338.5 nm in cyclohexane), while the species  $R-O-H \cdots OPy$  and  $R-O-H \cdots O(R)-H \cdots OPy$  are transparent in the same region. The constants are determined from the values of the optical absorptivities at ca. 338.5 nm for a large number (12 to 25) of dilute solutions of  $PyO$  and

$R-O-H$  (at different concentrations) in cyclohexane or carbon tetrachloride.

The experimental results at  $20.0 \pm 0.1$  °C are given in Table I, wherein the equilibrium constants, in the mole-fraction scale, are defined by eq 4-6. This table also shows

$$K_1 = x_{ROH \cdots OPy} / x_{ROH} x_{PyO} \quad (4)$$

$$K_2 = x_{(ROH)_2} / x_{(ROH)}^2 \quad (5)$$

$$K_3 = x_{(ROH)_2 \cdots OPy} / x_{(ROH)_2} x_{PyO} \quad (6)$$

that our results satisfactorily agree with the few available data from other sources.

### Discussion

(1) The constants in carbon tetrachloride are consistently smaller than those in cyclohexane, the effect being more conspicuous for  $K_1$  and  $K_3$ ; this suggests the possibility of interactions between  $PyO$  and carbon tetrachloride.<sup>8,23</sup>

(2) Given the low steric requirements of the oxygen atom of  $PyO$ , we can reasonably assume that the ranking of  $K_1$  values essentially reflects the influence of the inductive effect<sup>9a-c</sup> of the substituent,  $R$ , on the hydrogen bonding (HB) acidity of  $ROH$ . In fact, it turns out that the experimental results do follow the inductive order, but only roughly: thus, as shown in Table I, while the trifluoromethyl group substantially enhances the acidity,  $(K_1)_{(CF_3)_2CHOH} / (K_1)_{CF_3CH_2OH} = 7.1$  and  $(K_1)_{CF_3CH_2OH} / (K_1)_{MeOH}$

(6) Rao, C. N. R. *Trans. Faraday Soc.* 1975, 981.

(7) Liddel, U.; Becker, E. D. *Spectrochim. Acta* 1957, 10, 70.

(8) Regarding the interactions between electron donors and carbon tetrachloride, see, e.g., (a) Dumas, J.-M.; Geron, G.; Peurichard, H.; Gomel, M. *Bull. Soc. Chim. Fr.* 1976, 720. (b) Dumas, J.-M.; Peurichard, H.; Gomel, M. *J. Chem. Res., Synop.* 1978, 54. (c) Castagna, B.; Dumas, J.-M.; Guerin, M.; Gomel, M. *J. Chim. Phys.* 1973, 960. (d) Kuroi, T.; Gondo, Y.; Kuwabara, M.; Shimada, R.; Kanda, Y. *Bull. Chem. Soc. Jpn.* 1981, 54, 2243.

(9) See, e.g., (a) Levitt, L. S.; Widing, H. F. *Progr. Phys. Org. Chem.* 1976, 12, 119. (b) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, 1975; chapter 2; (c) Taft, R. W.; Taagepera, M.; Abboud, J.-L. M.; Wolf, J. F.; De Fries, D. J.; Hehre, W. J.; Bartness, J. E.; Mc Iver, Jr., R. T. *J. Am. Chem. Soc.* 1978, 100, 7765. (d) A linear relationship between  $\log K_1$  and the inductive substituent parameter  $\sigma_I$ , determined in the gas phase by the double proton transfer technique,<sup>9c</sup> can be established. The correlation coefficient is higher than 0.99, but the experimental points show a considerable scatter around the line. [The value  $\sigma_I = 0.42$  for  $(CF_3)_2CH$  has been kindly communicated to us by Professor R. W. Taft.]

(1) Université Cadi-Ayyad.

(2) Université de Bretagne Occidentale.

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

(b) Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* 1979, 349. *Ibid.* 1979, 1923. (c) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Progr. Phys. Org. Chem.* 1981, 13, 485.

(4) Jorgensen, W. L. *J. Am. Chem. Soc.* 1981, 103, 341. *Ibid.* 1981, 345.

(5) (a) Frange, B.; Abboud, J.-L. M.; Benamou, C.; Bellon, L. *Bull. Soc. Chim. Fr.* 1982, 1, 134. (b) Benamou, C.; Bellon, L.; C. R. *Hebd. Seances Acad. Sci.*, in press.

Table I. Equilibrium Constants for the Processes 1-3

alcohol	solvent	$K_1^a$	$K_2^a$	$K_3 \times 10^{-3a}$
CH <sub>3</sub> OH (1)	c-C <sub>6</sub> H <sub>12</sub>	234 ± 12 <sup>b</sup>	56 ± 9 <sup>b</sup>	2.37 ± 0.36 <sup>b</sup>
C <sub>2</sub> H <sub>5</sub> OH (2)	c-C <sub>6</sub> H <sub>12</sub>	175 ± 5 <sup>b</sup>	48 ± 7 <sup>b</sup>	1.69 ± 0.20 <sup>b</sup>
<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH (3)	c-C <sub>6</sub> H <sub>12</sub>	180 ± 6 <sup>b</sup>	47 ± 7 <sup>b</sup>	2.02 ± 0.28 <sup>b</sup>
<i>i</i> -C <sub>3</sub> H <sub>7</sub> OH (4)	c-C <sub>6</sub> H <sub>12</sub>	173 ± 5 <sup>b</sup>	39 ± 6 <sup>b</sup>	1.31 ± 0.18 <sup>b</sup>
<i>sec</i> -C <sub>4</sub> H <sub>9</sub> OH (5)	c-C <sub>6</sub> H <sub>12</sub>	160 ± 4 <sup>b</sup>	40 ± 6 <sup>b</sup>	2.05 ± 0.34 <sup>b</sup>
<i>t</i> -C <sub>4</sub> H <sub>9</sub> OH (6)	c-C <sub>6</sub> H <sub>12</sub>	167 ± 5 <sup>b</sup>	22 ± 3 <sup>b</sup>	1.41 ± 0.20 <sup>b</sup>
<i>t</i> -C <sub>5</sub> H <sub>11</sub> OH (7)	c-C <sub>6</sub> H <sub>12</sub>	168 ± 5 <sup>b</sup>	18 ± 3 <sup>b</sup>	0.92 ± 0.10 <sup>b</sup>
CF <sub>3</sub> CH <sub>2</sub> OH (8)	c-C <sub>6</sub> H <sub>12</sub>	(7.30 ± 0.37)10 <sup>3c</sup>		
(CF <sub>3</sub> ) <sub>2</sub> CHOH (9)	c-C <sub>6</sub> H <sub>12</sub>	(5.00 ± 0.25)10 <sup>4c</sup>		
CH <sub>3</sub> OH	CCl <sub>4</sub>	111 ± 3 <sup>b</sup>	32 ± 5 <sup>b</sup>	1.10 ± 0.13 <sup>b</sup>
<i>t</i> -C <sub>4</sub> H <sub>9</sub> OH	CCl <sub>4</sub>	68 ± 2 <sup>b</sup>	17 ± 3, <sup>b</sup> 17.2 <sup>d</sup> , 17.8 <sup>e</sup>	0.241 ± 0.033 <sup>b</sup>

<sup>a</sup> Values at 20.0 ± 0.1 °C, expressed in the mole-fraction scale. <sup>b</sup> This work. <sup>c</sup> From ref 5b. <sup>d</sup> From ref 6. The original value is given in liters per mole at 25 °C. The appropriate change of units has been carried out, and the temperature effect has been corrected using the dimerization enthalpy given by the authors. <sup>e</sup> From ref 7. This is actually the dimerization constant of *t*-C<sub>4</sub>H<sub>9</sub>OD. The original datum has been treated as in footnote *d*.

Table II. Structural Effects on the Ratios  $K_3/K_1$  and  $K_2/K_1$ 

alcohol	solvent	$K_3/K_1^a$	$K_2/K_1^a$
CH <sub>3</sub> OH (1)	c-C <sub>6</sub> H <sub>12</sub>	10.13	0.24
CH <sub>3</sub> CH <sub>2</sub> OH (2)	c-C <sub>6</sub> H <sub>12</sub>	9.66	0.27
<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH (3)	c-C <sub>6</sub> H <sub>12</sub>	11.2	0.26
<i>i</i> -C <sub>3</sub> H <sub>7</sub> OH (4)	c-C <sub>6</sub> H <sub>12</sub>	7.57	0.23
<i>sec</i> -C <sub>4</sub> H <sub>9</sub> OH (5)	c-C <sub>6</sub> H <sub>12</sub>	12.8	0.25
<i>t</i> -C <sub>4</sub> H <sub>9</sub> OH (6)	c-C <sub>6</sub> H <sub>12</sub>	8.44	0.13
<i>t</i> -C <sub>5</sub> H <sub>11</sub> OH (7)	c-C <sub>6</sub> H <sub>12</sub>	5.48	0.11
CH <sub>3</sub> OH	CCl <sub>4</sub>	9.91	0.28
<i>t</i> -C <sub>4</sub> H <sub>9</sub> OH	CCl <sub>4</sub>	3.54	0.25

<sup>a</sup> Defined in the text.

= 31.8, the  $K_1$ 's for EtOH, *n*-PrOH, *i*-PrOH, *s*-BuOH, *t*-BuOH, and *t*-AmOH are extremely close and some 37% smaller than  $(K_1)_{MeOH}$ .<sup>9d</sup>

(3) Previous studies on cyclic and acyclic aliphatic ethers,<sup>10</sup> R-O-R', have shown that substituent effects on the HB basicity of these compounds vs. phenols and other acids in cyclohexane are heavily dependent on steric factors, which frequently mask and even reverse the inductive order. Here, we can expect the HB basicity of monomeric alcohols to be somewhat less sensitive to steric effects, because of the very small contribution from the hydroxylic proton. In the dimerization process (2), however, both partners are subject to the steric influence of R, their common substituent. This should lead to a mutual enhancement of the steric hindrance to self-association. On the other hand, and because of their opposing actions on acidity and basicity, the already small differential inductive contributions should remain nearly constant throughout the series 1 to 7. This naive reasoning seems to be substantiated by the experimental values of  $K_2$  given in Table I, which are nicely correlated by Taft's steric parameter,<sup>11,12</sup>  $E_s$ , alone:

$$\log K_2 = 0.238(E_s)_R + 2.011$$

$$n = 7, r = 0.984$$

The structural effects on  $K_3$ , on the other hand, seem harder to unravel, probably because of the complexity of the interactions involved (which very likely also include

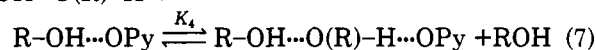
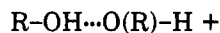
(10) Bellon, L.; Taft, R. W.; Abboud, J.-L. *M. J. Org. Chem.* 1980, 45, 1166.

(11) (a) Taft, Jr., R. W. In "Steric Effects in Organic Chemistry"; M. S. Newman, Ed.; Wiley: New York, 1956; chapter 13. (b) Unger, S. H.; Hansch, C. *Progr. Phys. Org. Chem.* 1976, 12, 91.

(12) All values are from ref 11b, except that for compound 7. We have estimated the  $E_s$  value for the *t*-C<sub>5</sub>H<sub>11</sub> group as  $(E_s)_{t-C_5H_{11}} = (E_s)_{t-C_4H_9} + [(E_s)_{n-Pr} - (E_s)_{Et}]$ .

dispersion forces)<sup>13</sup> and of the greater freedom of internal rotation within the R-OH...O(R)-H...OPy species. Some general trends clearly emerge, however: in all cases,  $K_3 > K_1$ . The ratio  $K_3/K_1$  is somewhat solvent dependent, as shown in Table II, and, in every case,  $(K_3/K_1)_{CCl_4} < (K_3/K_1)_{c-C_6H_{12}}$ . The results in cyclohexane—which are likely to be a more trustworthy measure of intrinsic structural effects—yield for the aliphatic alcohols 1-7 an average ratio  $K_3/K_1$  of ca. 10.

Let us consider at this point reaction 7 wherein ROH



and its dimer compete for one PyO molecule. The corresponding equilibrium constant,  $K_4$ , is a measure of the relative acidities toward PyO of the dimer and the monomer. It is easy to see that  $K_4 = K_3/K_1$ . We conclude that the dimers of these alcohols are, on the average, one order of magnitude more acidic toward PyO (in cyclohexane) than the corresponding monomers.

Equation 7 also describes the competition of the electron donors R-OH...OPy and R-OH for one R-OH molecule. Consequently,  $K_4 \approx 10$  measures the relative basicities of PyO...HO-R and R-OH toward R-OH.

This conclusively shows that when an R-OH molecule is simultaneously acting as hydrogen-bonding acceptor and donor at the same site, both the acidity and the basicity are enhanced relative to the same molecule acting only as acceptor or donor. This confirms Kamlet's earlier contentions<sup>16</sup> based on more indirect evidence. Similar phenomena have been reported for *n*-octanol<sup>17</sup> and for water.<sup>18</sup> Huyskens<sup>19</sup> has recently studied the HB association between a number of meta- and para-substituted phenols,

(13) There are several indications of these effects. Thus, according to Duboc,<sup>14</sup> the tetramerization constants for straight-chain aliphatic alcohols in carbon tetrachloride decrease on going from methanol to 1-butanol and then increase from 1-butanol to 1-octanol. Grunwald and co-workers (Grunwald, E.; Pan, K. C.; Effio, A. *J. Phys. Chem.* 1976, 27, 2937) have found the chains in 1-octanol to contain (at 25 °C) some 28 monomer units. This is a far greater number than in the cases of methanol and ethanol.<sup>4</sup> These experimental facts are well in line with theoretical estimates.<sup>15</sup>

(14) Duboc, C. *Spectrochim. Acta* 1974, 30A, 441.

(15) See, e.g., Buckingham, A. D. In "Organic Liquids: Structure, Dynamics and Chemical Properties", Buckingham, A. D.; Lippert, E.; Bratos, S., Eds.; Wiley-Interscience: New York, 1978; chapter 19.

(16) Kamlet, M. J.; Kayser, E. G.; Jones, M.-E.; Abboud, J.-L. M.; Eastes, J. W.; Taft, R. W. *J. Phys. Chem.* 1978, 82, 2477.

(17) Geisler, G.; Fruwert, J.; Stoeckel, E. *Z. Phys. Chem. (Wiesbaden)* 1962, 32, 330.

(18) Gordon, J. E. *J. Am. Chem. Soc.* 1972, 94, 650.

(19) Huyskens, P. L. *J. Am. Chem. Soc.* 1977, 99, 2579.

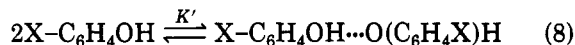
Table III. Self-Association Constants  $K_t$ ,  $K_d$ , and  $K_{dd}$  at 28 °C

alcohol	solvent	$K_t^{a,b,d}$	$K_d^{c,d}$	$K_{dd}^{c,d}$
CH <sub>3</sub> OH	CCl <sub>4</sub>	220	2.51	37.3
<i>t</i> -C <sub>4</sub> H <sub>9</sub> OH	CCl <sub>4</sub>	19	1.33	10.7

<sup>a</sup> In mole<sup>-3</sup>·L<sup>3</sup>. <sup>b</sup> From ref 14. <sup>c</sup> In mole<sup>-1</sup>·L.

<sup>d</sup> Defined in the text.

X-C<sub>6</sub>H<sub>4</sub>OH, and the nitrogen bases (B) triethylamine and tetramethylurea in carbon tetrachloride. In that work, the association constants  $K'$  and  $K''$  corresponding to the equilibria 8 and 9 were determined.

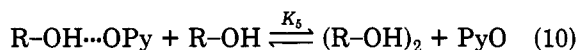


X-C<sub>6</sub>H<sub>4</sub>OH +

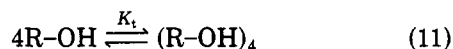


The ratio  $K''/K'$  is equivalent to the ratio  $K_3/K_1(K_4)$  of this study. It ranges from ca. 3 for the less acidic phenols to several hundred for the more acidic ones. For a given phenol, the stronger the base, the larger  $K''/K'$ . Although there is a resemblance between the patterns for alcohols and phenols, they cannot be directly compared because the proton acceptors are different.

For the less-hindered alcohols methanol and ethanol, we find  $K_2/K_1 \approx 0.25$ . This ratio is also the equilibrium constant  $K_5$  describing the competition between PyO and ROH for a single ROH molecule (eq 10) and measures the

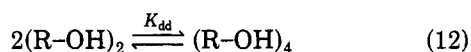
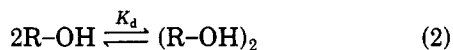


relative basicities of PyO and ROH toward ROH itself. Thus, not unexpectedly, the alcohols 1 to 7 appear as weaker bases than PyO. In the light of Huyskens' results, it can be inferred that the basicity of (ROH)<sub>2</sub> is intermediate between that of ROH and ROH⋯OPy. Quantitatively more precise conclusions can be drawn as follows: by means of IR spectrometry, Duboc<sup>14</sup> has succeeded in determining the constants  $K_t$  for the tetramerization reaction (eq 11) in carbon tetrachloride. Her values of  $K_t$



(in mol<sup>-3</sup>·L<sup>3</sup>) for MeOH and *t*-BuOH at 28 ± 3 °C are given in Table III, together with the corresponding values of the dimerization constants  $K_d$  (in mol<sup>-1</sup>·L) in the same solvent and at the same temperature (the  $K_d$ 's have been calculated from the values of  $K_2$  given in Table I after the appropriate change of units and correction of temperature effects using a blanket value of -5 kcal·mol<sup>-1</sup> for the dimerization enthalpies).

Let us consider the reactions shown by eq 2 and 12.



Equilibrium 2 is characterized by  $K_d = [(ROH)_2]/[ROH]^2$ , while  $K_{dd} = [(ROH)_4]/[(ROH)_2]^2$  pertains to equilibrium 12 (the concentrations of the various species in mol·L<sup>-1</sup> units). From the above equation we obtain eq 13, where

$$K_{dd} = K_t/K_d^2 \quad (13)$$

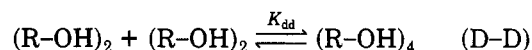
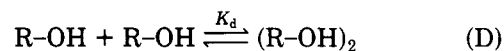
$K_{dd}$  represents the dimerization constants of the alcohol dimers. The values of  $K_{dd}$  are given in Table III. The availability of  $K_d$  and  $K_{dd}$  allows a direct comparison of the tendencies to self-association of monomers and dimers. It appears that, in both cases,  $K_{dd}$  is over one order of

magnitude more important than  $K_d$ . It seems, therefore, that we are witnessing the onset of "cooperative effects" which act as a driving force leading to extensive self-association in pure alcohols. Furthermore, considering again the couple MeOH/*t*-BuOH, we find  $(K_d)_{MeOH}/(K_d)_{t-BuOH} = 1.83$  and  $(K_{dd})_{MeOH}/(K_{dd})_{t-BuOH} = 3.49$ ; the main implication is that, although the constants  $K_d$  and  $K_{dd}$  taken separately are only moderately more favorable to MeOH than to *t*-BuOH, their selective effect builds up rapidly. Equation 13a, which is a straightforward consequence of eq 13, shows why it is so. We should expect a substantially

$$K_t = K_{dd}K_d^2 \quad (13a)$$

smaller concentration of species (R-OH)<sub>n</sub> with  $n > 6-7$  in *t*-BuOH than in MeOH. Also, the leading role played by steric effects in determining the ranking of the dimerization constants makes it likely that for the same value of  $n$  the (MeOH)<sub>n</sub> clusters be more stable than the (*t*-BuOH)<sub>n</sub> ones. These conclusions are in very good agreement with those drawn by Kamlet<sup>16</sup> and co-workers from their dilution studies.

Correlation analysis provides further insights into the mechanism of acidity enhancement through self-association. The dimerization (D) and tetramerization (D-D) are formally equivalent.



We might consider process D-D as a particular case of process D, wherein the acid R-OH is replaced by the acid (R-OH)<sub>2</sub>,  $f$  times stronger and the base ROH is replaced by the base (R-OH)<sub>2</sub>,  $g$  times stronger. Hence,

$$K_{dd} = K_d f g \quad (14)$$

Now, it can be shown<sup>20</sup> that if (ROH)<sub>2</sub> is  $f$  times more acidic than ROH toward the base ROH, it is also exactly  $f$  times more basic toward the acid ROH. It is therefore reasonable to take here  $f = g$ . This yields eq 14a, wherein

$$K_{dd} \approx K_d f^2 \quad (14a)$$

$f$  measures both the enhanced basicity and the enhanced acidity of (R-OH)<sub>2</sub> relative to ROH in the self-association process D-D. From the experimental values given above, we obtain  $f_{MeOH} = 3.9$  and  $f_{t-BuOH} = 2.84$ ; these are quite reasonable figures from the standpoint of our earlier discussion. Given that MeOH and *t*-BuOH are two rather extreme cases regarding bulk and chain branching, we can assume an average enhancement factor  $f$  of ca. 3.4 for basicity and acidity of (ROH)<sub>2</sub> relative to ROH (for alcohols 1 to 7). The closeness of the enhancement factors for MeOH and *t*-BuOH possibly reflects the opposing actions of the inductive effects within the moieties of the alcohol dimers. Equations 13 and 14 can be combined to give eq 15. The ratio  $(K_t)_{MeOH}/(K_t)_{t-BuOH}$  amounts to 11.6, while

$$K_t \approx K_d^3 f^2 \quad (15)$$

$f_{MeOH}^2/f_{t-BuOH}^2$  and  $(K_d)_{MeOH}^3/(K_d)_{t-BuOH}^3$  are, respectively, equal to 1.9 and 6.1. The excellent correlation between

(20) The proof is as follows: we consider the process (R-OH)<sub>2</sub> + R-OH  $\rightleftharpoons^{K_{tr}}$  (R-OH)<sub>3</sub> to which the equilibrium constant  $K_{tr}$  pertains. This reaction can be taken as the association between the proton donor (R-OH)<sub>2</sub>,  $f$  times stronger than R-OH, and the proton acceptor R-OH. We then have  $K_{tr} = K_d f$ . Alternatively, it can be viewed as the association between the proton donor R-OH and the proton acceptor (R-OH)<sub>2</sub>,  $g$  times stronger than R-OH. Hence,  $K_{tr} = K_d g$ . Either way,  $K_{tr}$  is the same and it follows that  $f = g$ .

$\log K_2$  and the steric parameter  $E_S$  (which is tantamount to a relationship between  $\log K_d$  and  $E_S$ ) implies that the ranking of  $K_d$ 's is essentially determined by steric factors. The  $f^2$  terms, on the other hand, are more likely to reflect electronic contributions. It is apparent, therefore, that the leading contribution to  $K_1$  (and most important, to the average size of the  $n$ -mers clusters) is heavily dependent on steric factors.

It is tempting to speculate about the relationships between these results and the properties of bulk alcohols. While scientific wisdom forbids rash extrapolations, some cautious inferences can be made: let us consider the strong HB base PyO dissolved in one of the aliphatic alcohols 1 to 7. Given the size of  $K_2$ ,  $K_1$ , and  $K_3$ , the concentration of monomers in the pure alcohol is very small and the solute will mostly interact with clusters. Those properties that characterize the HB acidity of bulk alcohols (such as the  $\alpha$  scale) actually describe the behavior of the clusters rather than that of the monomers. The equilibrium constants for the associations between the different clusters and PyO (taken as an example) in the neat alcohols are, in fact, unknown. It seems reasonable, however, that they be closer to  $K_3$  than to  $K_1$ . More precisely, let  $P$  be a solvent-dependent property of the solute and  $P_0$  its corresponding value in a medium devoid of HB acidity and endowed with a dipolarity<sup>21</sup> comparable to that of alcohols 1 to 7;  $P_{ROH}$  stands for the value of  $P$  in pure ROH. We believe that structural effects on the quantity  $P_{ROH} - P_0$  are more likely to be proportional to the quantity  $\log K_3$  (i.e., to the change in free energy for reaction 3) than to  $\log K_1$ . For alcohols 1 to 7 we tentatively suggest a relationship of the form shown in eq 16, where  $m$  is a proportionality constant.

$$P_{ROH} - P_0 = m \log (K_3)_{ROH} \quad (16)$$

The case of hexafluoro-2-propanol (9) seems quite different. This is so on account of (a) the considerable bulk of the chain and particularly (b) the very low basicity of the hydroxy group. These factors contribute to reduce the extent of self-association. Factor b should determine a very significant reduction of the acidity enhancement parameter  $f$  (which would be closer to one). Thus, for 9 we suggest eq 17. The behavior of trifluoroethanol (8) is the less

$$P_{(CF_3)_2CHOH} - P_0 = m \log (K_1)_{(CF_3)_2CHOH} \quad (17)$$

predictable of all because it lies between these two extremes. The fact that  $(K_1)_{CF_3CH_2OH}$  is much closer to  $(K_1)_{(CF_3)_2CHOH}$  than to  $(K_1)_{CH_3OH}$  hints at the possibility of  $P_{CF_3CH_2OH}$  being better described by an expression analogous to eq 17. We define an "apparent bulk constant"  $K_{app}$  such that  $K_{app} = K_3$  for alcohols 1-7 and  $K_{app} = K_1$  for alcohols 8 and 9. Figure 1 is a plot of  $\log K_{app}$  vs. the bulk acidity parameter for these materials.<sup>22</sup> The corresponding correlation equation is eq 18, with seven data

$$\log K_{app} = 2.200 + 1.242\alpha \quad (18)$$

points, a correlation coefficient,  $r = 0.9883$ , and a standard deviation of 0.085. The linear relationship thusly generated

(21) The bulk dipolarities of alcohols 1 to 7 fall within the 0.41-0.60 range in the  $\pi^*$  dipolarity scale.<sup>3c</sup>

(22) We have used  $\alpha = 1.45$  and 1.99 for  $CF_3CH_2OH$  and  $(CF_3)_2CHOH$ , respectively. We are most indebted to Professor R. W. Taft for communication of these data.

(23) A referee has pointed out that, in general, formation constants of hydrogen-bonded acid-base complexes decrease with increasing dipolarity-polarizability of the solvent. We agree with these vistas, which are fully compatible with the possibility of more specific solvent-solute interactions. We are most indebted to this referee for his valuable comments.

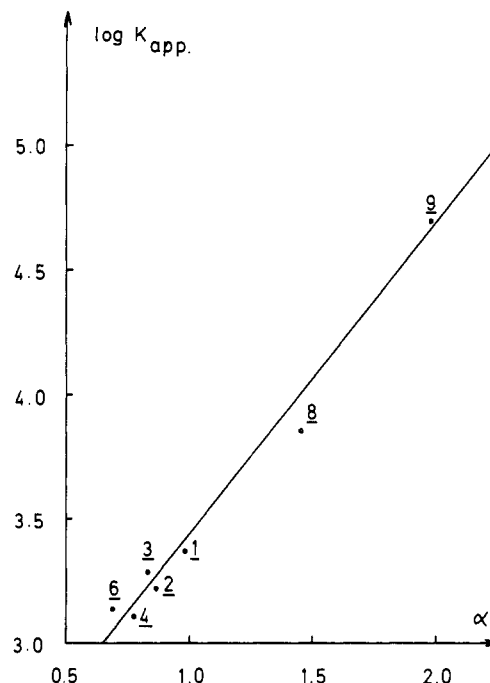


Figure 1.  $\log K_{app}$  in  $c\text{-C}_6\text{H}_{12}$  vs. HB acidity parameter  $\alpha$ .  $K_{app} = K_3$  for alcohols 1 to 7 and  $K_{app} = K_1$  for alcohols 8 and 9.

seems to support the likelihood of our hypothesis. This result might well be fortuitous, and great circumspection is necessary. Particularly, the use of  $K_{app}$  for linear solvation energy relationships involving bulk alcohols is definitely not recommended.

## Conclusion

This simple spectroscopic technique has allowed the determination of the dimerization constants in cyclohexane and carbon tetrachloride for several aliphatic alcohols. We have also measured the relative acidities vs. pyridine  $N$ -oxide of these molecules in their monomeric and dimeric forms. The combination of our data with Duboc's tetramerization constants has led to the direct quantitative evaluation of the effects of self-association upon the acidity and basicity of monomeric and dimeric alcohols. The fundamental role of steric hindrance in determining the strength and size of alcohols clusters has clearly emerged. These results also show promise in order to rationalize the empirical hydrogen-bonding acidity scale  $\alpha$ . This methodology can be easily extended to other self-associated acids.

## Experimental Section

The solvents cyclohexane and carbon tetrachloride were Merck "Uvasol" products, respectively, distilled from a Na-K alloy and  $P_2O_5$ . The alcohols were refluxed over and distilled from magnesium turnings. Pyridine  $N$ -oxide was crystallized in cyclohexane and twice sublimed (60-65 °C,  $5.0 \times 10^{-2}$  Torr) immediately prior to use. The measurements were performed with a Beckmann Acta V spectrophotometer with matched silica cells, 10-cm long.

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## Appendix

**Computational Technique.** At ca. 338.5 nm, the only absorbing species is PyO, while  $PyO \cdots HO-R$  and  $PyO \cdots (HO-R)_2$  are transparent. Let  $\Delta^0$  stand for the absorptivity of a highly dilute solution of PyO at this wavelength. Upon successive additions of alcohols, this absorptivity becomes  $\Delta^1, \Delta^2, \dots$  (after correction for dilution effects). Let  $\Delta^i$  be the absorptivity of the  $i$ th solution: it can be shown<sup>3a</sup> that

eq ES-1 holds, where  $x_A^i$  stands for the concentration of

$$\phi_i = (\Delta^0 - \Delta^i) / \Delta^i = K_1 x_A^i + K_2 K_3 (x_A^i)^2 \quad (\text{ES-1})$$

monomeric alcohol present in the solution. Since neither  $K_2$  nor the  $x_A^i$  are known off hand, an iterative minimax search for the optimal values of the constants is carried out. We have developed a program for the HP-41C programmable calculator which allows the determination of

these constants from the experimental absorptivities  $\Delta^i$  and the gross mole-fraction of the alcohol. The experimental values given in this work are the average of four to eight runs, each of them involving 12 to 25 solutions (i.e.,  $i = 12-25$ ).

**Supplementary Material Available:** Table of experimental  $x_i$  and  $\phi_i$  values and listing of the programs (7 pages). Ordering information is given on any current masthead page.

## Linear Solvation Energy Relationships. 14. Additions to and Correlations with the $\beta$ Scale of Hydrogen Bond Acceptor Basicities

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Existing literature data and new results are used with correlations reported earlier, as well as some new correlations first reported here, to determine  $\beta$  values of 90 additional liquid and solid hydrogen bond acceptor bases containing various types of functional groups as acceptor sites. Differences between "family independent (FI)" and "family dependent (FD)" correlations with  $\beta$  are demonstrated.

In earlier papers on the subject of linear solvation energy relationships (LSER's), we used a "solvatochromic comparison method" to unravel multiple solvent effects on many types of properties and rationalize them in terms of linear combinations of dependences on three indexes of solvent properties (the solvatochromic parameters). The  $\pi^*$  scale is an index of solvent dipolarity/polarizability which measures the ability of the medium to stabilize a charge or a dipole by virtue of its dielectric effect.<sup>1-4</sup> The  $\alpha$  scale of solvent hydrogen bond donor (HBD) acidities describes the solvent's ability to donate a proton in a solvent to solute hydrogen bond.<sup>1,5-7</sup> The  $\beta$  scale of hydrogen bond acceptor (HBA) basicities provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute to solvent hydrogen bond.<sup>1,8-11</sup> The  $\beta$  scale has also been used to evaluate hydrogen bond acceptor strengths of *solid* HBA bases dissolved in non-HBA solvents.<sup>10</sup> Rather than being based on solvent effects on single indicators, as has been the case for most earlier solvent property scales,<sup>12</sup> the solvatochromic pa-

rameters were arrived at by averaging normalized solvent effects on diverse properties of many types of indicators.

The solvatochromic parameters were intended for use in linear solvation energy relationships of the general form of eq 1 where  $\delta$ , a "polarizability correction term", is 0.0

$$\text{XYZ} = \text{XYZ}_0 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (1)$$

for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents.<sup>13a</sup> Numerous relatively precise LSER's have been reported wherein the XYZ term in eq 1 has been the logarithm of a reaction rate or equilibrium constant, a fluorescence lifetime or a GLC partition coefficient, a position or intensity of maximal absorption in an NMR, ESR, IR, or UV/visible absorption or fluorescence spectrum, an NMR coupling constant, or a free energy or enthalpy of solution or of transfer between solvents.

In practice it has proven quite difficult to disentangle the multiple solvent effects when all four solvatochromic parameters influenced the XYZ (primarily because of complications by type AB hydrogen bonding when both solvent and solute are amphiprotic).<sup>13b</sup> By judicious choices of solvents and/or reactants or indicators, however, it has usually been possible to exclude one or more of the terms in eq 1 and reduce it to a more manageable form.<sup>14</sup>

Thus, if XYZ is  $\nu_{\text{max}}$  or the transition energy of a  $\pi \rightarrow \pi^*$  electronic spectral transition, the  $d$  term is zero. For other properties, if consideration is limited to nonchlorinated aliphatic solvents, the  $\delta$  parameter is zero. In either case the  $d\delta$  term drops out. If the indicators or reactants are nonprotonic (and non Lewis acids),<sup>11</sup>  $b$  equals zero, and the  $b\beta$  term drops out. With protonic or Lewis acid reactants or indicators, correlations have usually been restricted to nonprotonic solvents for which the  $\alpha$  param-

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