perature for 2 h. After acidification and removal of EtOH in vacuo, the solution was extracted with Et_2O. The residue (3 mg) obtained from the organic phase, after evaporation of the solvent, was purified by TLC (SiO_2, using benzene–Et_2O (1:1) as the eluant) to yield **2** (2.5 mg), which without further purification was used to obtain the acetonide of **2** as described below. **2**: ^1H NMR δ 5.30 (1 H, m, H-6), 5.19 (1 H, m, H-15), 4.97 (1 H, m, H-7), 4.28 (2 H, AB q, H_2-18), 3.95 (1 H, m, H-3), 3.82 (1 H, m, H-2), 2.53 (1 H, m, H-4β), 2.27 (1 H, m, H-4α), 2.09 (3 H, s, CH_3CO), 2.00 (3 H, s, CH_3CO), 1.99 (3 H, s, CH_3CO), 1.07 (3 H, s, H_3-19), 1.06 (3 H, d, J = 7 Hz, H_3-21), 0.84 (6 H, d, J = 7 Hz, H_3-26 and H_3-27); mass spectrum, m/z 558 ($M^+ - H_2O$), 516 (M^+ – AcOH), 498 (M^+ – AcOH – H_2O).

Acetonide Formation from Sterol 2. **2** (2.5 mg) in dry acetone (0.5 mL) containing *p*-TsOH (1 mg) was stirred overnight at room temperature. The mixture was neutralized with $BaCO_3$ and centrifuged and the supernatant evaporated to dryness. The residue was then purifed by TLC (SiO_2, benzene–Et_2O (1:1)) thus obtaining the 2,3-acetonide of **2**: ^1H NMR δ 5.30 (1 H, m, H-6), 5.22 (1 H, m, H-15), 5.02 (1 H, m, H-7), 4.28 (2 H, AB q, H_2-18), 3.75 (2 H, m, H-3 and H-2), 2.09 (3 H, s, CH_3CO), 2.02 (3 H, s, CH_3CO), 2.01 (3 H, s, CH_3CO), 1.06 (3 H, s, H_3-19), 1.05 (3 H, d, J = 7 Hz, H_3-21), 0.84 (6 H, d, J = 7 Hz, H_3-26 and H_3-27); mass spectrum, m/z 541 (M^+ – AcOH – CH_3), 499 (M^+ – AcOH – CH_3 – 42).

Acknowledgment. This work was supported by Ministero della Pubblica Istruzione-Italia. We thank Dr. M. Pansini (Università di Genova-Italia) for identifying the hydroid. Mass spectral data were provided by Servizio di Spettrometria di Massa del C.N.R. e dell'Università di Napoli. The assistance of the staff is gratefully appreciated.

Registry No. 1, 96964-91-9; 2, 96964-92-0; 2 acetonide, 96964-93-1.

Studies on Amphiprotic Compounds. 2. Experimental Determination of the Hydrogen Bond Acceptor Basicities of "Monomeric" Alcohols[1]

José-Luis M. Abboud,*[2a,b] Khadija Sraidi,[2a] Georges Guiheneuf,[2a] Alfredo Negro,[2b] Mortimer J. Kamlet,*[2c] and Robert W. Taft[2d]

Département de Chimie, Faculté des Sciences, Université Cadi Ayyad, Marrakech, Morocco, Cátedra de Quimica, Facultad de Veterinaria, Universidad de Léon, 24004, Léon, Spain, Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland 20910, and Department of Chemistry, University of California, Irvine, California 92717

Received October 23, 1984

Equilibrium constants have been determined for the hydrogen-bonding association between 3,4-dinitrophenol (ArOH) and "monomer" alcohols (ROH) in highly dilute cyclohexane solutions. These data have been anchored

ArOH + HOR ⇌ ArOH•••OHR (R = Me, Et, *n*-Bu, *i*-Pr, *t*-Bu, 1-adamantyl)

to the empirical β scale of hydrogen bond acceptor basicities to yield the hitherto unavailable β_m parameters for the "monomeric" alcohols. These values have been compared with bulk solvent (mainly "oligomer") β values. The differential structural effects on the monomer acidities and basicities of the alcohols have been quantitatively analyzed in terms of field, resonance, and polarizability effects.

Alcohols, phenols, carboxylic acids, and amides are valuable solvents and reagents in organic chemistry, and these same functionalities are found in a wide variety of compounds of biological importance. A common feature of these species in their neat liquid forms or when acting as solvents is their extensive self-association through hydrogen bonding.[3] We have recently undertaken a program aimed at obtaining quantitative information on the hydrogen bond donor (HBD) acidities and hydrogen bond acceptor (HBA) basicities of these compounds in the "monomeric" forms they assume when acting as solutes. Such data should allow a more complete understanding of effects of structure and self-association on hydrogen-bonding interactions.

The empirical scales of solvent dipolarity/polarizability (π^*), HBD acidity (α), and HBA basicity (β) provide a good deal of information on non-self-associating compounds and on self-associating compounds in their "polymeric" forms, as well as a framework and methodology for the analysis of these data.[4] The recent extension of this methodology to the treatment of *solute* properties such as solubilities in water[5] and octanol/water partition coefficients[6] and the importance of including non-self-associated amphiprotic solutes in these linear solvation energy relationships further highlights the need to determine monomer HBA basicities (β_m) of such compounds.

Several methods, which lead to remarkably coincident values, are available for the determination of β values of HBA bases.[7] Certain of these techniques involve the use of solvatochromic indicators dissolved in the pure bases and, when applied to alcohols or other self-associated species, yield values measuring the average HBA basicities of the monomers and oligomers present in the bulk sol-

(1) Part 1: Frange, B.; Abboud, J.-L. M.; Benamou, C.; Bellon, L. *J. Org. Chem.* **1982**, *47*, 4553.
(2) (a) Université Cadi Ayyad. (b) Universidad de Léon. (c) Naval Surface Weapons Center. (d) University of California.
(3) For a recent comprehensive review on the self-association of alcohols, see: Symons, M. C. R. *Chem. Soc. Rev.* **1983**, *12*, 1.
(4) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.
(5) Taft, R. W.; Abraham, M. H.; Doherty, R. M.; Kamlet, M. J. *Nature (London)* **1985**, *313*, 384.
(6) (a) Kamlet, M. J.; Abraham, M. H.; Doherty, R. M.; Taft, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 464. (b) Taft, R. W.; Abraham, M. H.; Famini, G. R.; Doherty, R. M.; Abboud, J.-L. M.; Kamlet, M. J. *J. Pharm. Sci.*, in press.
(7) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485.

0022-3263/85/1950-2870$01.50/0

vent.[8] Clearly the study of monomeric alcohols requires a method involving highly dilute solutions of these compounds in "inert" (non-HBA base) solvents.

Let us consider the equilibrium between an HBD acid, AH, and a series of HBA bases, B_i, in an inert solvent:

$$AH + B_i \overset{K_{1i}}{\rightleftharpoons} AH\cdots B_i \quad (1)$$

In general, there is an excellent linear correlation between log K and β:

$$\log K_{1i} = a + b\beta_i \quad (2)$$

In many cases eq 2 has been used to generate β_i values (which have been averaged to obtain the reported β values),[4] and, in principle, it can be applied to alcohols. This, however, is not a straightforward operation when these equilibria are studied by spectroscopic techniques.

Let K_1 stand for the constant (in mole fraction units) corresponding to the equilibrium 3a:

$$AH + HOR \overset{K_1}{\rightleftharpoons} AH\cdots OHR \quad (3a)$$

We assume that AH and AH···OHR are the only radiation absorbing species. It can be shown[9] that the reliability of K_1 is critically dependent on the ratio, ρ, of the mole fractions of the associated and the free forms of AH, namely $(X_{AH\cdots B})/(X_{AH})$. Optimal values for ρ are in the range 1–2. From the law of mass action, we arrive at eq 4:

$$\rho = (X_{AH\cdots OHR})/(X_{AH}) = K_1 X_{ROH} \quad (4)$$

Equation 4 implies that, for a given proton donor, ρ can only increase by increasing X_{ROH}. However, even in dilute solution, equilibrium 3b can also become significant:

$$2ROH \overset{K_2}{\rightleftharpoons} (ROH)_2 \quad (3b)$$

Since monomeric alcohols are both less acidic and less basic than their dimers,[10] it follows that $(ROH)_2$ may compete with ROH for the association with AH:

$$AH + (ROH)_2 \overset{K_3}{\rightleftharpoons} AH\cdots O(R)H\cdots O(R)H \quad (3c)$$

The ratio $(X_{AH\cdots OHR})/(X_{AH\cdots(OHR)_2})$ can be expressed in terms of the equilibrium constants, K_1, K_2, and K_3:

$$(X_{AH\cdots(OHR)_2})/(X_{AH\cdots OHR}) = (K_3/K_1)K_2X_{ROH} = (K_2/K_1)(K_3/K_1)\rho \quad (5)$$

Equation 5 shows that any attempt to improve the precision in the measure of K_1 through an increase in ρ entails a proportional increase of the unwanted contribution from AH complexation with $(ROH)_2$. The ratio K_3/K_1 is always higher than unity[10] and K_2 depends only on the nature of the alcohol. Therefore, the only way to optimize the measurements is through the use of the strongest possible hydrogen-bond donors.

Several years ago, Bellon and Benizri[11] studied associations between the HBD acids, 3,5-dichlorophenol and *m*-nitrophenol, and a series of primary, secondary, and tertiary alcohols. Their experiments were carried out in dilute solutions in cyclohexane and isooctane. Recent work has provided values of K_2 for the same alcohols dissolved in cyclohexane,[1] and the results suggest that the data of Bellon and Benizri are likely to be somewhat affected by the phenol/alcohol-dimer complexation. We have attempted to overcome this difficulty by using an even stronger HBD acid; the choice was severely limited by the extremely low solubilities of strongly acidic phenols in cyclohexane and carbon tetrachloride. The best compromise between HBD acidity and solubility was 3,4-dinitrophenol.

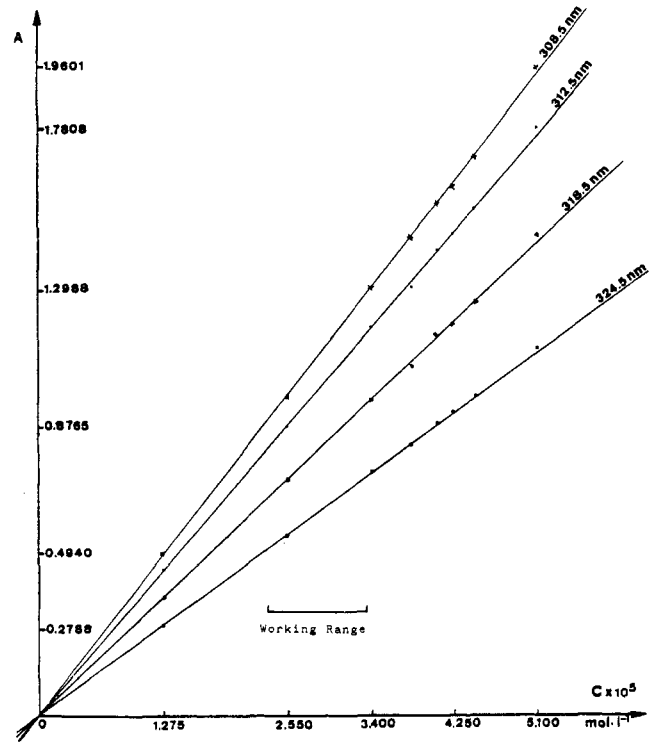

Figure 1. Absorbance of 3,4-dinitrophenol solutions (in c-C_6H_{12}) in 10-cm cells vs. concentration in mol L^{-1}. All experiments have been carried out in the "working range".

Table I. Equilibrium Constants for Monomeric Alcohols Involved in Reaction 3a[d]

alcohol solute	$10^{-3}K_1$[a]	μ,[b] D
methanol	1.41 ± 0.11	1.71
ethanol	2.62 ± 0.21	1.73
1-butanol	3.14 ± 0.25	1.81
2-propanol	4.25 ± 0.21	1.69
2-methyl-2-propanol	6.94 ± 0.35	1.67
1-adamantanol	12.8 ± 0.9	1.7[c]

[a] At 23.3 °C in cyclohexane. Values in the mole fraction scale. Each value is the average of at least six different measurements at various wavelengths in the range 302.5–319.5 nm. [b] Molecular dipole moments for these materials in the gas phase as given in ref 15. [c] Estimated. [d] AH is 3,4-dinitrophenol.

Experimental Results and Discussion

We have operated at 23.3 °C in cyclohexane solutions, and used standard UV–vis spectrophotometric techniques described elsewhere.[12] The initial mole fraction of the phenol was kept in the range of $(1.0–3.5) \times 10^{-6}$. A number of experiments carried out at wavelengths between 308.5 and 324.5 nm showed that the phenol solutions strictly follow the Beer–Lambert Law over, and even beyond, the mole fraction range used in this work. A plot of these results is shown in Figure 1. The gross mole fractions of the alcohols varied between 2.0×10^{-5} and 3.6×10^{-4}. The

(8) The complexity of the situation is clearly depicted by Symons and Eaton: Symons, M. C. R.; Eaton, G. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 3033.
(9) Derenleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044, 4050.
(10) (a) Reference 1. (b) Huyskens, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 2579. (c) Kamlet, M. J.; Kayser, E. G.; Jones, M. E.; Abboud, J.-L. M.; Taft, R. W. *J. Phys. Chem.* **1978**, *82*, 2477.
(11) Benizri, R.; Bellon, L. *Bull. Soc. Chim. Fr.* **1978**, *9*, 378.
(12) The experimental technique is a modification of that of: Nāgakura, S.: Baba, H. *J. Am. Chem. Soc.* **1952**, *74*, 5963. Nagakura, S.; Gouterman, M. *J. Chem. Phys.* **1957**, *26*, 881. See also: Bellon, L.; Taft, R. W.; Abboud, J.-L. M. *J. Org. Chem.* **1980**, *45*, 1166 and references therein.

Table II. Equilibrium Constants for HBA Bases Involved in Reaction 1[c]

solute base	$10^{-3}K_1$[a]	μ[b] D	β
$(n\text{-}C_4H_9)_2O$	1.14 ± 0.10	1.30	0.40
$(C_2H_5)_2O$	2.21 ± 0.13	1.30	0.47
tetrahydrofuran	5.30 ± 0.27	1.80	0.55
$ClCH_2COOC_2H_5$	1.40 ± 0.11	2.7	0.35
C_2H_5CN	3.52 ± 0.28	3.9	0.37
$(C_2H_5)_3N$	17.0 ± 1.4	0.70	0.71
$(n\text{-}C_3H_7)_3N$	12.8 ± 1.0	0.70	0.68
$HCON(CH_3)_2$	280 ± 13.0	3.8	0.69

[a] Same as for Table I. [b] Same as for Table I. [c] AH is 3,4-dinitrophenol

experimental formation constants of the 3,4-dinitrophenol/alcohol-monomer hydrogen-bonded complexes are given in Table I.

In order to anchor these data to the β scale by means of eq 2, we have determined the K_1 values for reaction 3a between 3,4-dinitrophenol and several non-self-associating bases at the same temperature (23.3 °C) and in the same solvent (c-C_6H_{12}). The results are summarized in Table II. A straightforward application of eq 2 yields eq 6:

$$\log K_1 = (1.61 \pm 0.67) + (4.19 \pm 1.23)\beta \quad n = 8,\ r = 0.812,\ \text{sd} = 0.49 \qquad (6)$$

The correlation coefficient is clearly too low and the standard deviation clearly too high by the usual standards of quality that we have applied to such correlations.

This result was not surprising to us, however, in the light of some earlier findings by Kamlet, Dickinson, Gramstad, and Taft[13] regarding contributions of dipolar effects to formation energies of a number of "hydrogen-bonded" complexes. These workers have shown that dipole/dipole interactions are dominant contributors to formation constants of HBA base complexes with diphenylamine and 4-bromoaniline in CCl_4 solvent and important (statistically significant) contributors to formation constants of complexes with 5-fluoroindole in CCl_4, chloroform in c-C_6H_{12}, tri-*n*-butylammonium ion in *o*-dichlorobenzene, and 4-fluorophenol in a number of solvents. Among the compounds studied, only in the case of the relatively less dipolar hydrogen-bond donor, trifluoroethanol, were contributions of dipole/dipole interactions to formation constants found to be statistically insignificant.

In view of the above and because 3,4-dinitrophenol has a dipole moment, μ, near 8 D (significantly higher than μ of any of the HBD acids studied earlier),[13,14] it seemed reasonable next to attempt a multiple parameter correlation of log K_1 with β and μ. Values of μ from McClellan's collection,[15] measured in the gas phase or in saturated hydrocarbon solvent, are included in Table II for the nonamphiprotic HBA bases; the multiple linear regression of log K_1 with β and μ is given by eq 6. This equation is

$$\log K_1 = (0.36 \pm 0.24) + (0.359 \pm 0.042)\mu + (5.19 \pm 0.36)\beta \quad n = 8,\ r = 0.989,\ \text{sd} = 0.135 \qquad (6)$$

clearly, by any standards, a high quality correlation, whose standard deviation compares favorably with the precision of the measurements. Further, the HBA bases used to generate eq 6 meet the following requirements: (i) the correlation between β and μ is low (r = 0.32); (ii) they span a reasonably wide range of β and μ values, while the K_1 values vary by well over 2 orders of magnitude.

Table III. β_m and β Values for Selected Alcohols

solute	β_m (β)
methanol	0.41_5 (0.62)
ethanol	0.47_0 (0.77)
n-butanol	0.48_0 (0.88)
2-propanol	0.51_0 (0.95)
2-methyl-2-propanol	0.56_0 (1.01)
1-adamantanol	0.60_0

It is of some interest to compare the relative weights of hydrogen-bonding and dipolarity contributions to log K_1 (i.e., to the change in free energy associated with process 3a). Considering propionitrile, a relatively weak base with an important dipole moment, we find that the dipolar contribution amounts to about 43% of the total effect. For Et_3N, this contribution drops to 13%. For the aliphatic monomer alcohols (vide infra), it amounts to 25%, a sizeable fraction.

HBA Basicities of Monomer Alcohols. We have used eq 6 with the log K_1 and μ values[15] in Table I to calculate β_m values for the alcohol monomers. These results, which are intended to apply to alcohol *solutes*, are assembled in Table III together with the "oligimer" β values, which are intended to apply to alcohol *bulk solvents*. [Due to possible complications by type-AB hydrogen bonding, wherein the indicator acts as both donor and acceptor (in a probably cyclic complex with two ROH molecules), the uncertainties in the latter β values are somewhat greater than for nonamphiprotic HBA solvents.][16] It is important to the subsequent discussion that the fractional dependence on μ does not influence the *relative* β_m values.

It is seen that the monomer β_m values are considerably smaller than the oligimer β values. This reflects the enhanced basicity of the alcohol clusters relative to the monomers, which we had earlier noted in our solvatochromic "dilution studies",[10c] and further confirms Huyskens observation[10b] that when an amphiprotic compound acts simultaneously as a hydrogen-bond acceptor and a hydrogen-bond donor at the same site, both the donor and the acceptor strengths are enhanced relative to the same species acting only as acceptor or only as donor.

Comparison with Alcohol Monomer HBD Acidities. The hydrogen-bonding association between monomeric alcohols and pyridine *N*-oxide (PyO) in dilute cyclohexane solutions, eq 7, has recently been studied with a view toward determining monomer HBD acidities.[1] It was found that, with the single exception of MeOH, only slightly more acidic than the other members of the family, K_4 is practically the same for EtOH, *n*-PrOH, *i*-PrOH, *t*-BuOH, and *t*-AmOH. This result is in sharp contrast with our present findings regarding basicity.

$$\text{ROH} + \text{PyO} \underset{}{\overset{K_4}{\rightleftharpoons}} \text{ROH}\cdots\text{OPy} \qquad (7)$$

Within the family of aliphatic alcohols, both field and resonance effects[17] (as measured by σ_F and σ_R) remain nearly constant, whereas the polarizability (as measured by σ_α)[17] steadily increases with the length and branching of the chain. It seems, therefore, that the main contribution to the differential structural effects originates in the polarizability of the aliphatic moieties. On this basis, it is tempting to conclude that the polarizability effect on HBA basicity is considerably greater than that on HBD

(13) Kamlet, M. J.; Dickinson, C.; Gramstad, T.; Taft, R. W. *J. Am. Chem. Soc.* **1982**, *47*, 4971.
(14) Estimated from data for 3,4-dinitroaniline, 4-nitroaniline, and 4-nitrophenol.
(15) McClellan, A. L. "Tables of Experimental Dipole Moments"; W. H. Freeman: San Francisco, 1963.
(16) See footnote on p 342 of: Kamlet, M. J.; Jones, M. E.; Taft, R. W.; Abboud, J.-L. M. *J. Chem. Soc., Perkin Trans 2* **1979**, 342.
(17) Headley, A.; Taagapera, M.; Koppel, I.; Taft, R. W. *J. Am. Chem. Soc.*, to be submitted.

acidity. At this point, the comparison of these results with those obtained in the gas phase is illuminating.

Ion cyclotron resonance spectroscopy (ICR) has allowed the determination of the free energies changes for reactions 8 and 9 in the gas phase.[18] It turns out that process 8 is,

$$ROH_2^+ + MeOH \rightleftarrows ROH + MeOH_2^+ \quad (8)$$

$$RO^- + MeOH \rightleftarrows ROH + MeO^- \quad (9)$$

indeed, about 2 times more sensitive to the polarizability of R than is process 9, i.e., relative effects similar to those in eq 3a and 7.

A further factor needs to be considered: The free energy changes in equilibrium 7 involve both "dipolar" and hydrogen-bonding contributions, very much like in the case of eq 3a. The molecular dipole moment of PyO is 4.2 D,[19] which might lead one to believe that the dipolar contribution to eq 7 would be relatively less important. In fact, it is likely to be the other way around. This is because the HBA site of PyO, the oxygen end of the NO group, is the locus of the main bond moment of the molecule. On the other hand, the two nitro groups in 3,4-dinitrophenol are much farther removed from the alcohol molecule. Thus, inasmuch as the dipole moments of the aliphatic alcohols are practically the same, K_4 provides a trustworthy ranking of their HBD acidities, but the high weight of the dipolar contributions might overshadow very minor structural effects.

Comparison of Hydrogen Bonding with Gas-Phase Proton Transfer. Given the conditions of very nearly constant field and resonance effects prevailing in processes 8 and 10 for alkanols, it is fair to compare the free energy

$$ArOH\cdots OHR + MeOH \rightleftarrows ArOH\cdots OHMe + ROH \quad (10)$$

changes associated with both processes, eq 11. The slope

$$\Delta G^\circ_{(10)} = -0.026 + 0.080\Delta G^\circ_{(8)}$$
$$n = 5,\ r = 0.99 \quad (11)$$

of eq 11 tends to suggest a low degree of proton transfer in reaction 10 (or 3a). Thus, in a process with low steric requirements, taking place in a medium unfavorable to charge dispersal, it is possible to find "gas-phase-like" behavior, even with only a modest degree of charge development.

(18) See footnote 35 of: Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 247; unpublished results.

(19) Grunwald, M.; Szafran, M.; Kreglewski, M. *Adv. Mol. Relax. Interact. Processes* **1980**, *18*, 53.

It the latter respect, it is of interest that 1-adamantanol appears to be a somewhat stronger base than 2-methyl-2-propanol, in agreement with their relative gas-phase basicities. Furthermore, Taylor and co-workers[20] have studied the gas-phase pyrolysis of 1-arylethyl acetates, eq 12, as well as the detritiation equilibrium in anhydrous

$$p\text{-}RC_6H_4CH(OAc)CH_3 \rightarrow p\text{-}RC_6H_4CH{=}CH_2 + HOAc \quad (12)$$

$$p\text{-}RC_6H_4T + CF_3COOH \rightleftarrows p\text{-}RC_6H_4H + CF_3COOT \quad (13)$$

trifluoroacetic acid given by eq 13. In both cases, bulky substituents such as bicyclo[2.2.2]octan-1-yl and adamantan-1-yl outperformed *tert*-butyl at stabilizing positive charge in the transition states. Although Taylor et al. have suggested that carbon–carbon hyperconjugation is the basis for these effects, our present results suggest that polarizability is a very important factor to take into consideration.

Experimental Section

The UV–vis experiments were performed at Université Cadi Ayyad with a Cary 219 spectrophotometer. Direct digital readout was used throughout. The solutions were contained in 10-cm matched cells. The stock solutions were prepared by weight and volumetrically. Successive additions of small volumes (100–400 μL) of dilute solutions of the HBA bases used an Amel electronic microburette accurate to 1 μL.

Merck Uvasol cyclohexane was refluxed over and distilled from P_2O_5. All alcohols were first refluxed over and distilled from calcium hydride. Methanol and ethanol were further dried by refluxing with magnesium/iodine. *n*-Butanol, 2-propanol, and 2-methyl-2-propanol were stored over 4-Å molecular sieves and distilled over magnesium turnings. 1-Adamantanol was sublimed twice. Wet 3,4-dinitrophenol (Fluka) was vacuum-dried (60 °C, 10^{-1} torr) and then column chromatographed over silica gel (Merck) and eluted with benzene/acetic acid (1:2). After vacuum removal of the eluent, the phenol was dissolved in dry Et_2O and slowly precipitated with *n*-hexane (ACS reagent grade). The central crop was collected and washed twice with boiling spectrograde cyclohexane. All other compounds, of the highest commercial purity, were treated by standard methods.

Registry No. THF, 109-99-9; 3,4-$(NO_2)_2C_6H_3OH$, 577-71-9; MeOH, 67-56-1; EtOH, 64-17-5; *n*-BuOH, 71-36-3; *i*-PrOH, 67-63-0; *t*-BuOH, 75-65-0; *n*-Bu_2O, 142-96-1; Et_2O, 60-29-7; $ClCH_2C(O)OEt$, 105-39-5; CH_3CH_2CN, 107-12-0; Et_3N, 121-44-8; *n*-Pr_3N, 102-69-2; $HC(O)NMe_2$, 68-12-2; 1-adamantanol, 768-95-6.

(20) Archer, W. J.; Hossaini, M. A.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1982**, 181 and references therein.