General Procedure. The reactions were carried out in a 0.1-L stirred autoclave (Sotelem) operating in a batch mode and equipped with a system for sampling of liquid during the course of the reaction.

The experimental procedure was as follows. The autoclave was charged with the freshly calcined zeolite (500 mg) or $AlCl_3$ (1 g) and the carboxylic acid (**1**, 5×10^{-3} mol) together with the aromatic compound (50 cm^3) and heated at 150 °C during 48 h. Under these conditions, the reactions follow pseudo-first-order kinetics. The products isolated by column chromatography on alumina with cyclohexane/ether (95:5) as eluent were identified by ^{13}C and ^{1}H NMR and by GLC–mass spectrography.

For competitive reactions, the autoclave was charged as previously described, using a mixture of benzene and toluene (50:50) as solvent. Samples were withdrawn periodically and analysed with gas–liquid chromatography. Relative rate constants can be determined by measuring the relative concentrations of the products. It was verified that the concentrations of products were in a constant ratio, independent of time.

Registry No. PhMe, 108-88-3; p-$Me_2C_6H_4$, 106-42-3; CH_3CO_2H, 64-19-7; $CH_3CH_2CO_2H$, 79-09-4; $CH_3(CH_2)_2CO_2H$, 107-92-6; $CH_3(CH_2)_4CO_2H$, 142-62-1; $CH_3(CH_2)_6CO_2H$, 124-07-2; $CH_3(CH_2)_{10}CO_2H$, 143-07-7; $CH_3(CH_2)_{14}CO_2H$, 57-10-3; $CH_3(CH_2)_{20}CO_2H$, 112-85-6; $CH_3C(O)$-p-C_6H_4Me, 122-00-9; $CH_3CH_2C(O)$-p-C_6H_4Me, 5337-93-9; $CH_3(CH_2)_2C(O)$-p-C_6H_4Me, 4160-52-5; $CH_3(CH_2)_4C(O)$-p-C_6H_4Me, 1669-33-6; $CH_3(CH_2)_6C(O)$-p-C_6H_4Me, 51770-83-3; $CH_3(CH_2)_{10}C(O)$-p-C_6H_4Me, 50671-19-7; $CH_3(CH_2)_{14}C(O)$-p-C_6H_4Me, 2657-10-5; $CH_3(CH_2)_{20}C(O)$-p-C_6H_4Me, 101493-90-7; 1-(2,5-dimethylphenyl)ethanone, 2142-73-6; 1-(2,5-dimethylphenyl)-1-propanone, 35031-52-8; 1-(2,5-dimethylphenyl)-1-butanone, 35031-53-9; 1-(2,5-dimethylphenyl)-1-hexanone, 17424-48-5; 1-(2,5-dimethylphenyl)-1-octanone, 101493-87-2; 1-(2,5-dimethylphenyl)-1-dodecanone, 101493-88-3; 1-(2,5-dimethylphenyl)-1-hexadecanone, 101493-89-4; 1-(2,5-dimethylphenyl)-1-docosanone, 101493-91-8.

Linear Solvation Energy Relationships. 40. A Reexamination of ^{13}C NMR Shifts and ^{13}C–^{19}F Coupling Constants of Trifluoroacetic Acid Complexes with Hydrogen Bond Acceptor Bases

Mikael Begtrup,* Robert W. Taft,* and Mortimer J. Kamlet*

Department of Organic Chemistry, The Technical University of Denmark, DK-2800 Lyngby, Denmark, Department of Chemistry, University of California, Irvine, California 92717, and Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland 20910

Received October 29, 1985

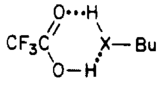
One of us has recently reported[1] an analysis of NMR spectral data of complexes of trifluoroacetic acid with hydrogen bond acceptor bases in CCl_4. ^{13}C Shifts of the carbonyl and CF_3 carbons and $^{1}J_{CF}$ and $^{2}J_{CF}$ coupling constants were determined for a number of n-butyl derivatives, n-BuX (X = Cl, CH=CH_2, CH=O, OH, SH, COOH, NO_2, etc.), and rationalized in terms of *linear solvation energy relationships* of the form of eq 1. The

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta + e\xi \qquad (1)$$

π^*, α, and β terms in eq 1 are the *solvatochromic parameters* that measure molecular dipolarity/polarizability, HBD (hydrogen bond donor) acidity, and HBA (hydrogen bond acceptor) basicity.[2] The ξ term is a *coordinate covalency* parameter[3] that has been used in conjunction with the β parameter to correlate and rationalize certain "family-dependent" basicity properties, i.e., properties (like aqueous pK_a) that are linear with β within families of bases having similar HBA sites (double-bonded oxygen bases, single-bonded oxygen bases, pyridine bases, sp^3-bybridized amine bases) but not between families. The equations of the form of eq 1 were then used to estimate new β_i values which were averaged to arrive at β values for some additional n-BuX derivatives. The β_i values from the different equations showed only modest agreement with one another and with β values estimated earlier by other methods.[2]

At the time the paper dealing with the $CF_3COOH{\cdot}HBA$ complexes appeared,[1] there were in the press three papers, coauthored by the other authors of the present paper,[3-5] that had a direct bearing on this study in a number of regards. (a) First, it was shown[3] that NMR shifts of HBA base complexes with trifluoroethanol, 4-fluorophenol, and 5-fluoroindole are family-independent properties, which are linear with β for all types of HBA bases without the intervention of the ξ parameter. The same is likely to be true of CF_3COOH complexes. (b) More importantly, it was also shown[4,5] that π^*, α, and β values of amphihydrogen bonding compounds are different depending on whether they are self-associated solvents or non-self-associated "monomer" solutes in dilute solutions. Thus, the π^* and β values of n-BuOH solvent are 0.47 and 0.88,[2] whereas the "monomer" π^*_m and β_m values are 0.40 and 0.45.[4] Under the conditions of the measurements discussed here (1.0 M CF_3COOH and 1.0 M HBA base in CCl_4), however, the n-BuX compounds, where X = OH, COOH, and SH, are unlikely to be either fully dissociated, as in more dilute solutions, or as fully associated as in the neat solvents. It would follow, therefore, that neither the π^*, α, and β nor the π^*_m, α_m, and β_m parameters are completely appropriate to describe the properties of the complexes with these amphihydrogen bonding solutes. (c) Finally, from solubility data in water and from octanol/water partition coefficients, we have been able to estimate[4] a number of additional β values which are germane to the present study.

Even if the NMR studies had been carried out at solute concentrations sufficiently low that the amphihydrogen bonding compounds would be "monomeric", another effect, not addressed in sufficient detail in any of our earlier LSER papers, would be likely to further complicate the correlations. This involves the likelihood of type AB hydrogen bonding, wherein both species involved act simultaneously as both HBD acids and HBA bases in a probably cyclic complex.[6] For n-BuXH and CF_3COOH, type AB hydrogen bonding would be represented by I. Strengths and effects of type AB hydrogen bonds are generally different than would be predicted from the summation of $a\alpha$ and $b\beta$ terms in eq 1.



I, X = O, S

For the above reasons we have now combined our efforts in order to reexamine and reinterpret the results of the NMR studies. Data for n-BuX compounds for which the solvatochromic parameters are known or can be estimated reliably (from corresponding values for closely related compounds), but excluding the results for X = OH, SH,

---

(1) Begtrup, M. *Acta Chem. Scand., Ser. A* **1985**, *A39*, 117.

(2) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

(3) Kamlet, M. J.; Gal, J. F.; Maria, P. C.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2*, in press.

(4) Taft, R. W.; Abraham, M. H.; Doherty, R. M.; Kamlet, M. J. *Nature (London)* **1985**, *313*, 384.

(5) Kamlet, M. J.; Abraham, M. H.; Doherty, R. M.; Taft, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 461. Taft, R. W.; Abraham, M. H.; Famini, G. R.; Doherty, R. M.; Kamlet, M. J. *J. Pharm. Sci.* **1985**, *74*, 807.

(6) Kamlet, M. J.; Taft, R. W., unpublished information.

0022-3263/86/1951-2130$01.50/0

Table I. Correlations of NMR Shifts and Coupling Constants of Trifluoroacetic Acid Complexes of HBA Bases in CCl_4

no.	X in substrate *n*-BuX	π^{*b}	β^b	$\delta_{C=O}$	δ_{CF_3}	$^1J_{CF_2}$	$^2J_{CF_3}$
1	*n*-Bu	−0.08	0.00	163.47	114.79	283.6	43.0
2	Cl	0.39	0.00	163.04	114.80	283.6	43.2
3	$CH=CH_2$	0.08	0.07[c]	163.01	114.83	285.1	43.3
4	NO_2	0.75	0.25	160.38	115.05	285.4	42.7
5	SCH_3	0.34	0.26[c]	160.35	115.05	285.1	42.2
6	$CH=O$	0.60	0.41	159.22	115.28	286.3	42.6
7	$COCH_3$	0.65	0.48	158.72	115.34	286.5	43.6
8	$COOCH_3$	0.50	0.45	158.81	115.39	286.5	41.7
9	OCH_3	0.27	0.48	158.69	115.44	285.8	41.8
10	CN	0.65	0.35	158.65	115.30	285.9	41.9

[a] HBA bases in 1.0 M solution in CCl_4 containing 1 mol equiv of CF_3COOH. [b] Most π^* and β values were estimated from corresponding values for related compounds (usually lower homologues). [c] Kamlet, M. J.; Doherty, R. M.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Pharm. Sci.*, in press.

Table II. Estimation of New β Values

no.	X in substrate *n*-BuX	est. π^*	$\delta_{C=O}$	β_1	δ_{CF_3}	β_2	β_3	β_{av}
1	SO_2Me	0.85	158.65	0.41	115.31	0.42		0.42
2	$SCOCF_3$	0.30	162.09	0.11	114.89	0.10		0.11
3	$OCOCF_3$	0.35	161.58	0.16	114.93	0.12	(0.19)[b]	0.16
4	$OCSCH_3$	0.40	160.69	0.25	115.08	0.24		0.25
5	$SCOCH_3$	0.40	159.11	0.43	115.27	0.38	0.43[a]	0.41
6	$SCSCH_3$	0.30	161.43	0.18	114.98	0.16		0.17

[a] From equation for $RCOCH_3$ compounds: $\beta = 0.40 - 0.56\sigma_I - 0.20\sigma_{R^+}$.[2] [b] Value reported[2] for ethyl trifluoroacetate.

and COOH, are assembled in Table I, as are the relevant π^* and β values of the HBA bases. Because the hydrogen bond donor compounds are excluded and because we are dealing with family-independent properties, we do not include the α and ξ parameters, and correlations are by eq 2.

$$XYZ = XYZ_0 + s\pi^* + b\beta \qquad (2)$$

The correlations by eq 2 for the $\delta_{C=O}$ and δ_{CF_3} ^{13}C shifts are given by eq 3 and 4. As expected, the effects of base HBA basicity and dipolarity/polarizability are greater for the carbon atom closer to the hydrogen bonding site. The

$$\delta_{C=O} = (163.48 \pm 0.23) - (1.40 \pm 0.54)\pi^* - (8.91 \pm 0.78)\beta \text{ ppm} \qquad (3)$$

$$n = 10,\ r = 0.9869,\ \text{sd} = 0.336 \text{ ppm}$$

$$\delta_{CF_3} = (114.77 \pm 0.03) - (0.02 \pm 0.07)\pi^* + (1.32 \pm 0.12)\beta \text{ ppm} \qquad (4)$$

$$n = 10,\ r = 0.9829,\ \text{sd} = 0.053 \text{ ppm}$$

precision of eq 3 and 4 is sufficiently good that we can use them to back calculate new β values. The insignificant dependence on π^* in eq 4 is of particular interest, because it allows a back calculation that is independent of our estimate of this parameter. The statistical quality of the correlation equations for the coupling constants, eq 5 and 6, is significantly poorer, and we now consider these results to be inadequate for back calculational purposes.

$$^1J_{CF} = (283.88 \pm 0.28) + (0.44 \pm 0.65)\pi^* + (4.76 \pm 0.95)\beta \text{ Hz} \qquad (5)$$

$$n = 10,\ r = 0.9315,\ \text{sd} = 0.44 \text{ Hz}$$

$$^2J_{CF} = (43.02 \pm 0.41) + (0.35 \pm 0.98)\pi^* - (2.06 \pm 1.42)\beta \text{ Hz} \qquad (6)$$

$$n = 10,\ r = 0.513,\ \text{sd} = 0.66 \text{ Hz}$$

β_i values back-calculated from eq 3 and 4 are assembled in Table II, together with several β_i values from other sources and resulting average β values for a number of additional *n*-BuX derivatives. Table II contains no surprises. Thus, Abboud[7] has determined β values of 0.40 and 0.55 for $HCSNMe_2$ and $Me_2NCSNMe_2$, compared with 0.69 and 0.80 for $HCONMe_2$ and $Me_2NCONMe_2$, i.e., decreases of 0.29 and 0.25 on replacing C=O by C=S. These accord reasonably well with the β_{av} values of 0.25 for $BuOCSCH_3$ compared with 0.45 for $BuOCOCH_3$ and of 0.17 for $BuSCSCH_3$ compared with 0.41 for $BuSCOCH_3$. The β_i values for $BuSCOCH_3$ agree quite well with a value calculated from an earlier reported[2] multiple substituent parameter equation for β of R_1COR_2 compounds (the latter β_i being included in the β_{av} result).

Registry No. $CH_3(CH_2)_6CH_3$, 111-65-9; BuCl, 109-69-3; $CH_3(CH_2))_3CH=CH_2$, 592-41-6; $BuNO_2$, 627-05-4; $BuSCH_3$, 628-29-5; $CH_3(CH_2)_3CHO$, 110-62-3; $CH_3(CH_2)_3COCH_3$, 591-78-6; $CH_3(CH_2)_3COOCH_3$, 624-24-8; $BuOCH_3$, 628-28-4; $CH_3(CH_2)_3CN$, 110-59-8; $BuSO_2Me$, 2976-98-9; $BuSC(O)CF_3$, 760-47-4; $BuOC(O)CF_3$, 367-64-6; $BuOC(S)CH_3$, 55613-69-9; $BuSC(O)CH_3$, 928-47-2; $BuSC(S)CH_3$, 69380-59-2; CF_3CO_2H, 76-05-1.

---

(7) Prof. J.-L. M. Abboud, Universidad de Leon, private communication.

Acid-Catalyzed Hydrolysis of Benzophenone Crown Ether Acetals and Analogous Open Chain Acetals

Shinya Ueno, Takumi Oshima, and Toshikazu Nagai*

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan

Received November 12, 1985

The hydrolysis of acetals has received much attention in recent years.[1,2] The generally accepted mechanism involves a fast preequilibrium protonation of the acetal,

---

(1) (a) Cordes, E. H. *Progr. Phys. Org. Chem.* **1967**, *4*, 1. (b) Cordes, E. H.; Bull, H. G. *Chem. Rev.* **1974**, *74*, 581.

(2) (a) Bergstrom, R. G. In *The Chemistry of Ethers, Crown Ethers, Hydroxy Groups and Their Sulphur Analogues*; Patai, S., Ed.; Wiley: Chichester, 1980; Chapter 20. (b) Burt, R. A.; Chiang, Y.; Kresge, J. *Can. J. Chem.* **1980**, *58*, 2199. (c) Jensen, J. L.; Carr, M. D.; Yamaguchi, K. S. *Int. J. Chem. Kinet.* **1983**, *15*, 235.

0022-3263/86/1951-2131$01.50/0