Catalysis Letters 31 (1995) 351–358

Evaluation of hydrogen bonding ability of liquids and solids by C-13 NMR. Silica gel as a strong hydrogen bond donor

Dan Fărcaşiu [1] and Anca Ghenciu

Department of Chemical and Petroleum Engineering, University of Pittsburgh, 1249 Benedum Hall, Pittsburgh, PA 15261, USA

Received 11 November 1994; accepted 11 January 1995

The chemical shift difference between signals of C(β) and C(α) of unsaturated ketones, $\Delta\delta$, which we used before to measure acid strengths, has now been used to evaluate the hydrogen bond donor ability of solvents which are not acidic enough to hydronate the indicator. For such solvents there is no general correlation between H-bond donor ability and acid strength: hexafluoroisopropanol is a much weaker acid than acetic acid, but it is a stronger H-bond donor. The method can be applied to evaluate the H-bonding properties of solid surfaces, and it was thus found that silica gel has a much stronger H-bond donor ability than methanol or acetic acid.

Keywords: hydrogen bonding, measurement by NMR; NMR, hydrogen bonding evaluation by; solids, hydrogen bonding ability of; solvents, hydrogen bonding ability of; supports, hydrogen bonding ability of

1. Introduction

In previous papers we reported on a method of acidity measurement using ^{13}C NMR spectroscopy, which can be used on working strong acid catalysts not amenable to traditional Hammett acidity measurements based on UV–visible spectroscopy [1]. Our method requires the use of an indicator base for which the positive charge acquired upon hydronation [#1] is distributed very unevenly between carbon atoms. α,β-unsaturated ketones (**1**) proved to be useful for this purpose. Upon hydronation,

[1] To whom correspondence should be addressed.

[#1] The use of "hydron" was recommended to distinguish the ion of H in natural composition from the isotopic species "proton", "deuteron", and "triton", see ref. [2].

$$\underset{\mathbf{1}}{RCH_2-CO-\overset{\alpha}{C}H=\overset{\beta}{C}R'-Me} + AH \rightleftharpoons \underset{\mathbf{2}}{RCH_2-C(OH)=\overset{\alpha}{C}H-\overset{\beta}{C}^{+}R'-Me} + A^{-}, \quad (1)$$

a: R = H, R′ = Me

most of the positive charge in the conjugate acid **2** is localized in the β position; the α position carries little charge. Therefore, our method [#2] uses the chemical shift difference $\Delta\delta$ between the signals for C(β) and C(α),

$$\Delta\delta = \delta_{C(\beta)} - \delta_{C(\alpha)}, \quad (2)$$

as a measure of the extent of hydronation free of solvent effects [1,3]. Because the acid–base equilibrium of eq. (1) is fast, the chemical shifts of the ^{13}C NMR signals for the mixture of **1** and **2** are the weighted average of the values for the two species and are a measure of the extent of hydronation (ratio **2**/**1**). As this quantity varies linearly with the total concentration of indicator in dilute solutions [1,4], an acidity function can be derived by the use of the chemical shift difference at infinite dilution, $\Delta\delta^0$ [1],

$$\Delta\delta = s([B] + [BH^+]) + \Delta\delta^0. \quad (3)$$

A calibration of $\Delta\delta^0$ with the Hammett acidity H_0 of sulfuric acid solutions allows the determination of this acidity function for other acids [1].

Our approach has been checked and validated by the examination of a large number of strong acid solutions. Thus, we determined H_0 values for molecular acids (perchloric, phosphoric, methanesulfonic), as well as for complex and composite acid catalysts, such as BF_3–H_2O [5], $MeSO_3H$–P_2O_5 (Eaton catalyst [6]) [7], BF_3–H_3PO_4–H_2O [8], and a heteropolyacid in solution [9]. Information about the structure of and reactions occurring within complex acids has also been obtained from these measurements [7–9]. H_0 values were obtained even for "dirty" acid catalysts from industrial installations, not characterizable otherwise [1b]. Moreover, other researchers have applied our method, to correlate the acid strength of the catalysts with reaction rates in the Fischer indole synthesis [10] and to assess the acid strength of H-ZSM-5 zeolite [11].

In our previous work, we noticed a variation of $\Delta\delta$ and $\Delta\delta^0$ with the solvent even for acid solutions where hydronation of mesityl oxide was very small or negligible (3–4 H_0 units weaker than required for half-hydronation of **1a**). This behavior was not related to the polarity of solvent, because $\Delta\delta$ was the same in chloroform and DMSO, but it was manifested by solvents with OH groups which can form hydrogen bonds [1]. Based on the values measured in MeOH, AcOH, and dichloroacetic acid we concluded tentatively that the hydrogen bonding increases with the solvent acidity in the H_0 range where no significant hydron transfer occurs and that $\Delta\delta$ can be used to compare the acidity of these media, even though their

[#2] The same approach was used before in ref. [3].

H_0 values cannot be deduced [1b]. We have since verified on other compounds this correlation of hydrogen bond donor ability of solvents in the absence of hydronation with their acid strength and found it incorrect. We found, however, that these measurements can provide a comparison of hydrogen bond donor ability of solvents which are not strong enough acids to donate a hydron to the indicator in measurable amount. Moreover, using the sample of silica gel, we found that we can evaluate the H-bond donor ability of solid surfaces carrying OH groups. This property can be important for the use of these materials as supports for catalysts. We report our results here.

2. Experimental

2.1. MATERIALS

HFIP 98% was used as received and handled in a nitrogen-filled glove bag. Sulfolane was redistilled over P_2O_5 under reduced pressure. SO_2 (b.p.= -10°C) and neopentane (b.p.= 9.5°C) were used as received, but were transferred into the vacuum line through a P_2O_5 column for drying. Silica gel (Davisil, grade 634, 100–200 mesh, 60 Å, surface area 480 m^2/g, pore volume 0.75 cm^3/g) was dried overnight at 130°C for all the samples. A second type of silica gel (Merck, 35–70 mesh, 40 Å, surface area 675 m^2/g, pore volume 0.68 cm^3/g) was used for some experiments after the same treatment. For the experiments in acetic acid, several drops of acetic anhydride were added to the acid (less than 1%), to avoid traces of moisture.

Mesityl oxide 98%, was checked by GC and used without any further purification.

2.2. SAMPLE PREPARATION

All the liquid samples were prepared in preweighed 8 mm NMR tubes as described previously [1]. The samples in sulfolane and HFIP were handled in a nitrogen-filled glove bag. Samples in SO_2 were run in sealed tubes as described elsewhere [12].

Ketone **1a** was deposited on silica gel (ca. 1 g dry solid, weighed on an analytical balance, 1/10 mg weighing precision) from neopentane. Freon 11 and dichloromethane were also examined as solvents. The NMR spectra were not significantly different, but the entrainment was somewhat higher, especially for the latter. Neopentane was, like SO_2, distilled on the vacuum line through a column containing P_2O_5 and was collected into a two-necked round-bottomed flask containing a preweighed amount of dry silica gel and a stirring bar. **1a** was added with a syringe through a septum, with stirring. Its quantity was determined by weighing the syringe before and after the addition. After 2–3 min of stirring, the solvent was removed by distillation and the amount of **1a** deposited was checked by weighing

the flask. Although the difference between the boiling points of **1a** and the solvent is large, traces of **1a** were lost by evaporation with the solvent, and traces of solvent remained on the solid, as shown by the NMR spectrum.

2.3. NMR MEASUREMENTS

All the experiments in solution have been performed under the same conditions as described before [1]. The silica gel samples were run with magic angle spinning on the same instrument [1], in 7 mm zirconia rotors, at a spinning rate of 2500 rps. A high power proton decoupling pulse sequence (HPPD) [13], with phase alternation was used with 90° pulse (5.2 μs), a recycle delay of 8 s, and decoupling during excitation and acquisition (49 ms). The chemical shifts were measured from a calibration spectrum of adamantane as standard (low-field signal at 38.2 ppm).

3. Results and discussion

Table 1 presents $\Delta\delta$ values obtained for mesityl oxide (**1a**) in several solvents, as a function of concentration. Where only one value is given, no variation with concentration was seen. The first impression that $\Delta\delta^0$ follows the order of acidity (entries 6 and 7) is contradicted by the results on hexafluoroisopropanol (HFIP, entry 8). This solvent has a low acidity ($pK_a = 9.3$ [14]), but it is known as a very strong hydrogen bond donor [#3], a property which led to its practical application as catalyst promoter [16]. The $\Delta\delta^0$ value of **1a** in HFIP (39.35 ppm) is significantly greater than in the much stronger acid, AcOH (33.84 ppm, $pK_a = 4.75$ [17a]).

The way to distinguish between hydrogen bonding and hydronation of the indicator (eq. (1)) is by examining the value of the correlation slope s in eq. (3). The changes in s for solutions where the indicator is hydronated to a measurable extent and their significance, were discussed in our earlier publications [1]. For any particular acid the value of s varies with the acid strength, exhibiting a minimum (largest negative value) for the acid which hydronates the indicator to an extent of 50% [1]. At low acidity, the base is only slightly hydronated and $\Delta\delta$ changes little with the concentration of base. For practical purposes, we may consider that a value of s less negative than -0.5 indicates that hydronation is negligible and the interaction is mere hydrogen bonding. In early studies of acidity by NMR spectroscopy it was found that hydrogen bonding from the acid alters the hydronation curves of alcohols, ethers, carboxylic acids, and amides [3b]. Our results show that the $\Delta\delta$ parameter can be used to rank the hydrogen bond donor ability of solvents too weak to hydronate the indicators **1** to a significant amount. It is noteworthy that these measurements show again the exceptional hydrogen bond donor properties of HFIP as solvent mentioned above [15,16].

[#3] For a discussion and pertinent references, see ref. [15].

Table 1
Chemical shifts of mesityl oxide (**1a**) in different solvents

	Solvent	Conc. of **1a**		Chemical shift (ppm)			s [a]
		mol/ ℓ solution	mol **1a**/ mol solvent	$\delta_{C(\alpha)}$	$\delta_{C(\beta)}$	$\Delta\delta = \delta_{C(\beta)} - \delta_{C(\alpha)}$	
1	none					29.70	
2	$CDCl_3$ [b]	0.79				30.70	
3	DMSO [b]	0.79				30.71	
4	SO_2	0.5		125.75	158.17	32.42	
5	sulfolane	0.79		124.55	154.70	30.15	
6	CH_3OH [b]	0.79				32.16	
7	AA [c]	1.45	0.10	124.39	157.81	33.42	
		0.43	0.03	124.36	158.07	33.71	
		0.22	0.01	124.36	158.13	33.77	
		0.02	0.002	124.36	158.20	33.84	
		0.00	0.00			33.84	−0.29
8	HFIP	0.98	0.11	123.39	162.28	38.89	
		0.46	0.05	123.36	162.49	39.13	
		0.24	0.03	123.33	162.57	39.24	−0.48
		0.00	0.00			39.35	

[a] Slope s in eq. (3).
[b] From ref. [1], recorded at 22.65 MHz, from internal TMS at 0.00; ppm [1].
[c] AA: acetic acid, $H_0 = 0.0$ [26].

Silica has been reported as catalyst in many organic reactions [#4] [18] and as catalyst support in a number of applications [#5] [19–23]. It appeared of interest to us to determine the hydrogen bond donor ability of the OH groups on its surface.

As catalytic material, silica gel has been described in literature as having very weakly acidic sites. By titration with various bases, the pK_a value was determined as 6.8 [24a], 7.1 ± 0.6 [24b], and by spectroscopic measurements, 7.1 ± 0.5 [24c]. Other studies of silica (Cab-O-Sil) [25] showed that no acid sites, either Brønsted or Lewis, exist on the surface. Pyridine is attached to the surface by hydrogen bonds [26], and ammonia is only physisorbed on silica surface [27]. Nonetheless, some authors claimed that silica gel contains sites of H_0 between −3 and 6.8 [28a], or between H_0 1.5 and 4.8 [28b]. It is likely that materials reported in literature as

[#4] For a summary of the use of silica gel as catalyst, see ref. [18a].
[#5] For acid and base catalysis: see ref. [19a] for H_3BO_3, H_3PO_4, H_2SO_4 on silica gel; see ref. [19b] for NaOH and KOH on silica. For Fischer–Tropsch catalysts, metals/SiO_2, see ref. [20]. For partial oxidation of methane on V or Mo oxides/silica, see ref. [21]. For olefin metathesis: WO_3, Re_2O_7, or MoO_3/SiO_2, see ref. [22]. For surface studies of metal/SiO_2 catalysts: Ni–Cu/SiO_2, see ref. [23a]; Rh/SiO_2, see ref. [23b].

Table 2
Chemical shifts of mesityl oxide (**1a**) on silica gel

Silica gel	Concentration of **1a**		Chemical shift (ppm)		
	mmol **1a**/ g dry solid	x [a]	$\delta_{C(\beta)}$	$\delta_{C(\alpha)}$	$\Delta\delta = \delta_{C(\beta)} - \delta_{C(\alpha)}$
Davisil	8.25	1.46	154.74	124.44	30.30
	5.02	0.89	155.04	124.34	30.70
	3.17 [b]	0.55	155.84	124.40	31.44
	1.10	0.19	157.95	124.27	33.68
	0.58	0.10	158.87	124.21	34.66
	0.31	0.06	159.44	124.18	35.26
	0.16	0.03	159.84	123.77	36.07
	0.00	0.00			36.20 [c]
Merck	4.57	0.55	155.18	124.41	30.77
	4.03	0.49	155.50	124.41	30.99
	2.43	0.29	156.21	124.45	31.76

[a] x = fraction of a monolayer of **1a**.
[b] The values here were 3.17 ± 0.08, because of a greater weighing error in this experiment.
[c] Extrapolated from values at 1.1, 0.58, 0.31, and 0.16 mmol **1a** per gram of solid.

"silica" contained variable amounts of extraneous acidic species adsorbed, which means that the catalytic properties observed were not due to the silica itself. To avoid such pitfalls, we employed a silica gel from Davisil, described as "of pH 6.5", together with another material, made by Merck. In our hands, both silica gels gave a slurry with distilled water of pH ≥ 6.4 (bromocresol purple indicator $pK_a = 6.4$ [17b]). The chemical shifts of **1a** on silica gel (dried first at 130°C) at various levels of surface coverage are shown in table 2. It can be seen that the OH groups on the surface have a hydrogen bond donor ability between those of acetic acid and HFIP. It is also seen that the $\Delta\delta$ values increase as the coverage level is decreased, even below the monolayer coverage. Extrapolation to zero coverage gives $\Delta\delta^0 = 36.204$ ppm. This could mean either that **1a** migrates fast over the surface, such that it behaves like in solution, or, more likely, that there is a non-uniform distribution of hydrogen bond donor ability over the surface. As the coverage decreases, **1a** is adsorbed preferentially on sites (pores, cracks) where stronger or multiple H-bonds are formed.

Our results show that silica gel is a strong hydrogen bond donor. It is uncertain whether this property is important in its application as support for metal catalysts, but it should have consequences for its use as support for metal oxides [21,22].

Acknowledgement

This work has been supported by a grant (CTS-9121454) from NSF.

References

[1] (a) D. Fărcaşiu, A. Ghenciu and G. Miller, J. Catal. 134 (1992) 118;
(b) D. Fărcaşiu and A. Ghenciu, J. Am. Chem. Soc. 115 (1993) 10901.
[2] J.F. Bunnett and R.A.Y. Jones, Pure Appl. Chem. 60 (1988) 1115.
[3] (a) B.P. Dailey and J.N. Shoolery, J. Am. Chem. Soc. 77 (1955) 3977;
(b) J.T. Edward, J.B. Leane and I.C. Wang, Can. J. Chem. 40 (1962) 1521;
(c) D.G. Lee, Can. J. Chem. 48 (1970) 1919.
[4] D. Fărcaşiu and A. Ghenciu, J. Org. Chem. 56 (1991) 6050.
[5] D. Fărcaşiu and A. Ghenciu, J. Catal. 134 (1992) 126.
[6] P.E. Eaton, G.R. Carlson and J.T. Lee, J. Org. Chem. 38 (1973) 4071.
[7] D. Fărcaşiu and H. Cao, J. Mol. Catal. 87 (1994) 215.
[8] D. Fărcaşiu and J.Q. Li, J. Phys. Chem. 98 (1994) 6893.
[9] D. Fărcaşiu and J.Q. Li, J. Catal., in print.
[10] D.L. Hughes, J. Phys. Org. Chem., in print.
[11] T. Xu, E.J. Munson and J.F. Haw, J. Am. Chem. Soc. 116 (1994) 1962.
[12] D. Fărcaşiu, S.L. Fisk, M.T. Melchior and K.D. Rose, J. Org. Chem 47 (1982) 453.
[13] D.L. VanderHart, W.L. Earl and A.N. Garroway, J. Magn. Res. 44 (1981) 361;
A. Pines, M.G. Gibby and J.S. Waugh, J. Chem. Phys. 59 (1973) 569.
[14] A.S. Tracey, B. Gallefi and S. Mahjour, Can. J. Chem. 66 (1988) 2294.
[15] D. Fărcaşiu, J. Jähme and C. Rüchardt, J. Am. Chem. Soc. 107 (1985) 5717.
[16] D. Fărcaşiu, US Patents 4,585,750 (1986); 4,673,769 (1987); 4,677,090 (1987).
[17] *Handbook of Chemistry and Physics*, 72rd Ed. (CRC Press, Boca Raton, 1991) (a) p. 8-39; (b) p. 8-14.
[18] (a) A. McKillop and D.W. Young, Synthesis (1979) 401;
(b) K. Smith, ed., *Solid Supports and Catalysts in Organic Synthesis*, Organic Chemistry Series (Horwood PTR Prentice Hall, 1992) pp. 95–96.
[19] (a) H.A. Benesi, J. Am. Chem. Soc. 78 (1956) 5490;
(b) K. Tanabe, *Solids Acids and Bases – Their Catalytic Properties* (Kodansha/Academic Press, Tokyo/New York) p. 2.
[20] B.W. Wojciechowski, Catal. Rev. Sci. Eng. 30 (1988) 629;
M.A. Vannice, J. Catal. 37 (1975) 462.
[21] H.-F. Liu, R.-S. Liu, K.Y. Liew, R.E. Johnson and J.H. Lunsford, J. Am. Chem. Soc. 106 (1984) 4117;
K.J. Zhen, M.M. Khan, C.H. Mak, K.B. Lewis and G.A. Somorjai, J. Catal. 94 (1985) 501.
[22] V.D. Drăguţan, A.T. Balaban and M. Dimonie, *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins* (Wiley Interscience, New York, 1985).
[23] (a) S.D. Robertson, B.D. McNicol, J.H. de Baas, S.C. Kloet and J.W. Jenkins, J. Catal. 37 (1975) 424;
(b) G. Galleher, J.G. Goodwin, Jr., C.-S. Huang and M. Houalla, J. Catal. 127 (1991) 719; 140 (1993) 453.
[24] (a) P. Schindler and H.R. Kamber, Helv. Chim. Acta 51 (1968) 1781;
(b) D.N. Strazhesko, V.B. Strelko, V.N. Belyakov and C. Rubank, J. Chromatography 102 (1974) 191;
(c) M.L. Hair and W. Hertl, J. Phys. Chem. 74 (1970) 91.
[25] K. Tanabe, M. Misono, Y. Ono and H. Hattori, in: *New Solid Acids and Bases – Their Catalytic Properties*, Studies in Surface Science and Catalysis, eds. B. Delmon and J.T. Yates (Kodansha/Elsevier, Tokyo/Amsterdam, 1989) pp. 93–102.
[26] E.P. Parry, J. Catal. 2 (1963) 371.
[27] J.E. Mapes and R.R. Eischens, J. Phys. Chem. 58 (1954) 809.

[28] (a) T. Yamaguchi and K. Tanabe, Bull. Chem. Soc. Jpn. 47 (1974) 424;
(b) K. Shibata, T. Kiyoura, J. Kitagawa, T. Sumyioshi and K. Tanabe, Bull. Chem. Soc. Jpn. 46 (1973) 2985.
[29] C. Rochester, *Acidity Functions*, Organic Chemistry Series, Vol. 17 (Academic Press, New York, 1970) p. 22.