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Absence of correlation of hydrogen bond donor ability with acid strength and catalytic activity of acid catalysts

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Two liquids, acetic acid and hexafluoroisopropanol (HFIP), and two solids, silica gel and polymethacrylic acid (PMA), were compared for hydrogen bond donor ability, acid strength, and catalytic activity in typical acid-catalyzed reactions, inversion of sugar and cleavage of acetone dimethyl ketal. In each pair, the weaker acid (HFIP and silica gel, respectively) was much the stronger hydrogen bond donor, but was totally devoid of catalytic activity, which the poor hydrogen bond donor but stronger acids (acetic and methacrylic acid, respectively) exhibited. A strong hydrogen bond donor (e.g., HFIP) enhances, however, the catalytic activity of the acid catalyst (AcOH). Thus, hydrogen bond donor ability is not a measure of acid strength. A correlation of the two properties is possible only when each group (acids and bases) involved in the comparison consists of very close structural relatives. Such a correlation cannot be extrapolated to any other case.

Keywords: acid strength and catalytic activity, acid strength and H-bond donor strength, catalytic activity and acid strength, catalytic activity and H-bond donor strength, H-bond donor strength and acid strength, H-bond donor strength and catalytic activity

1. Introduction

It is generally understood that in acid catalysis there is a direct relationship between the acid strength of the catalyst and the rate of the catalyzed reaction [1]. Failure of this correlation strongly suggests that the activation of the substrate involves another type of reaction than hydron[1] transfer [3]. Measurement and calibration of catalyst acidity becomes, therefore, important for understanding mechanisms and for development of new catalysts and processes. Typically, the acid strength is measured from the interaction of the acid with a probe base of known basic strength [4]. It was found that the results of such measurements are adequate for correlation with catalytic activity when the probe base is similar in the nature of its reactivity with the intended catalytic substrate [5].

The normal acid–base reaction is preceded by the formation of a hydrogen-bonded complex between acid and base (equation (1)). Obviously, hydrogen bonding is possible for p-bases (e.g., N and O bases) and π-bases (alkenes and aromatics), but not when the acid cleaves a C–H bond [6] or C–C bond [6c,d,7] in a saturated hydrocarbon [6e,8].

$$\mathrm{AH} + \mathrm{B} \rightleftharpoons \mathrm{A{-}H}\cdots\mathrm{B} \tag{1}$$

$$\mathrm{A{-}H}\cdots\mathrm{B} \rightleftharpoons \mathrm{A}^{-}\cdots\mathrm{H}^{+}\mathrm{{-}B} \tag{2}$$

$$\mathrm{A}^{-}\cdots\mathrm{H}^{+}\mathrm{{-}B} \rightleftharpoons \mathrm{A}^{-} + \mathrm{B{-}H}^{+} \tag{3}$$

In non-polar media, the acid–base interaction consists of an equilibrium between a hydrogen-bonded acid–base pair and a hydrogen-bonded ion pair (equation (2)). The latter may dissociate in a separate step (equation (3)) [9]. The catalytic reaction does not require the dissociation step, because the conversion of the substrate can occur, and in the case of the solid acids has to occur, in the tight ion pair [3]. On the other hand, preliminary complexation is not necessary in hydroxylic solvents, where the acid and the base are individually hydrogen-bonded with the solvent, and the hydron transfer can be relayed by the solvent, without the collision of the reactants [1b,10].

Because the hydrogen bond formation (equation (1)) is the preliminary step of hydron transfer (equation (2)), it has been considered that the strength of hydrogen bonding (the position of the equilibrium in equation (1)) toward some standard acceptor should be a measure of the strength of the acid [4b,11]. For such a measurement, the acceptor must be a base too weak to be hydronated to any measurable extent by the acid as in equation (2). We have argued against this interpretation, maintaining that there is no general correlation of hydrogen bond strength and acid strength [10,12]. We have now conducted experiments comparing the hydrogen bond donor ability of some liquids and solids with their activity as catalysts for acid-catalyzed reactions and report our findings here.

2. Experimental

2.1. General

Crosslinked polymethacrylic acid (PMA) was obtained as the moisture-saturated H-form from Scientific Polymer Products, Inc., TGA (40–150 °C at 10 °C/min) gave a 26%

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[1] The name “hydron” has been recommended for the positive ion of H in natural isotopic composition, to be distinguished from the isotopically pure species “proton”, “deuteron”, and “triton”, see [2].

weight loss. For drying, the polymer (30 g) was covered with anhydrous methanol (30 ml) in an Erlenmeyer flask containing a Teflon-coated stirring bar, stoppered by a ground-joint stopper, and stirred for 30 min at 40 °C. The methanol was then decanted off, and the operation was repeated three more times with fresh solvent each time. The slurry was filtered with suction and the solid was dried in a convection oven at 60 °C for 20 min, then in a vacuum oven at 70 °C and 2 Torr for 12 h. TGA, conducted as described above, gave a weight loss of 1.5%.

Silica gel (Davisil, grade 634, 100–200 mesh, surface area 480 m^2, pore volume 0.75 cm^3/g), hexafluoroisopropanol (HFIP), acetic acid (AcOH), sulfur dioxide, and mesityl oxide (MES) were treated and handled exactly as described earlier [13]. The catalytic substrates, 2,2-dimethoxypropane (Aldrich) and glucose (Baker), and the GLC integration standards, 3-methylpentane (Alfa) and 2,3-dimethylpentane (Wiley Organics), were of the highest grade available and were used as purchased.

MES was deposited onto PMA from liquid sulfur dioxide, on a vacuum line [13]. The NMR experiments were conducted in the same way as in our previous work [13a], but on a DMX300 instrument.

*2.2. Solvolysis of 2,2-dimethoxypropane (**1**)*

(a) *In acetic acid (AcOH)*. Glacial acetic acid (3.0 ml, 52.5 mmol), the ketal **1** (1.29 ml, 10.5 mmol), and 3-methylpentane (0.1 ml, integration standard) were introduced into a 10 ml tube provided with a screw-cap with a septum, pre-thermostated at 58 °C. Samples were taken with a microsyringe through the septum during the reaction and were analyzed by GLC on a 4.5 m × 3 mm OD column packed with 10% silicone SP2100 on 80–100 mesh Supelcoport, held for 12 min at 30 °C, then heated to 35 °C at 10 °C/min and held there for 20 min. The products were identified by GC-MS with the same instrument and column as in an earlier study [3].

(b) *In HFIP*. The reaction mixture consisted of HFIP (5.5 ml, 52.5 mmol), **1** (1.29 ml, 10.5 mmol), and 2,3-dimethylpentane (0.1 ml) as integration standard. The procedure was the same as for the reaction in AcOH.

(c) *In a mixture of AA and HFIP*. The reactant **1** (1.2 ml, 9.75 mmol) was mixed with HFIP (1.7 ml, 16 mmol), AcOH (1.5 ml, 26.5 mmol), and 3-methylpentane (0.1 ml). The reaction was run and the mixture was analyzed as in the previous experiments.

2.3. Hydrolysis of sucrose

Sucrose (20 g, 23 mmol) was dissolved in water (50 ml) and 50 ml of this solution was introduced into a two-necked round-bottomed flask equipped with a magnetic stirring bar, stoppered, and brought to the desired temperature in a thermostated oil bath. The solid, PMA or silica gel (5 g), was introduced at once and the flask was stoppered again. To monitor the progress of the reaction, samples were withdrawn and analyzed by polarimetry, with a Carl Zeiss polarimeter at room temperature. The last sample in each batch was somewhat turbid and was filtered before analysis.

3. Results and discussion

Two pairs of materials were compared for hydrogen bond donor ability and catalytic activity in typical acid-catalyzed reactions: one pair of liquids, AcOH and HFIP, and one pair of solids, PMA and silica gel. To establish the relative hydrogen bond donor ability, we employed the NMR chemical shift difference at infinite dilution, $\Delta\delta^0$, with mesityl oxide as the hydrogen bond donor acceptor, as described in our earlier publications [4b,13a]. The results are presented in table 1.

Acetic acid (pK_a 4.75 [14], H_0 0.0 [15]) is a weak acid and HFIP (pK_a 9.3 [16]) is a very weak acid, at least in aqueous solution. Furthermore, based on the established relationship between the strength of solid acids and acids in solution [17], we evaluate PMA as being significantly weaker than AcOH. Silica gel has no acidic properties, or it is, at most, an extremely weak acid [13]. Therefore, none of these materials should hydronate to any measurable extent mesityl oxide, which is half-hydronated in a medium of H_0 between -4.0 and -4.5 [4c]. The sizable differences in $\Delta\delta^0$ observed, 5.5 units between HFIP and AcOH, 6.5 units between silica gel and PMA, represent, therefore, only the differences in the hydrogen bond donor abilities of these materials. Whereas the pair, for which some acid strength parameters were available (pK_a values in water solution, for AcOH and HFIP), exhibited an inverse relationship between acidity and hydrogen bond donor ability, the ultimate proof of existence or absence of such a correlation [4b,11] could be offered only by a comparison of their catalytic activity.

We selected for the study two reactions, for which the A1 mechanism (specific acid catalysis, equations (4)–(7))

Table 1

Chemical shifts of mesityl oxide (MES) in solution and on solid surfaces.

Solvent or solid adsorbent	Concentration of MES	$\Delta\delta$[a]
AcOH[b]	0.10[c]	33.42
	0.03	33.71
	0.01	33.77
	0.002	33.84
	0.00	33.84[d,e]
HFIP[f]	0.00[c]	39.35[d,g]
PMA[h]	0.68[i]	29.38
	0.55	29.39
	0.31	29.53
	0.18	29.63
	0.00	29.71[j]
Silica gel[f]	0.00[k]	36.20[d,l]

[a] $\Delta\delta = \delta_{C(\beta)} - \delta_{C(\alpha)}$ for MES ($Me_2C^{\beta}{=}C^{\alpha}H–CO–Me$). [b] From [13b]. [c] Mol/mol of solvent. [d] $\Delta\delta^0$, from $\Delta\delta = s \times \mathrm{Conc(MES)} + \Delta\delta^0$. [e] $s = -0.29$. [f] From [13a]. [g] $s = -0.48$. [h] This work. [i] Mol/mol of –COOH groups in the polymer. [j] $s = -0.53$. [k] mmol/g of dry solid. [l] $s = -2.38$.

had been firmly established: solvolysis of 2,2-dimethoxypropane (acetone methyl ketal, **1**) [18] and hydrolysis ("inversion") of sucrose [19]. In each of these reactions, a fast, reversible hydronation is followed by rate-determining unimolecular dissociation and fast trapping of the intermediate by the solvent (SOH). The actual catalyst in equation (4) can, however, be the conjugate acid of the solvent, $\mathrm{SOH_2^+}$.

$$\mathrm{R{-}X + A{-}H \rightleftharpoons R{-}X{-}H^+ \cdots A^-} \quad \text{(fast)} \tag{4}$$

$$\mathrm{R{-}X{-}H^+ \cdots A^- \rightarrow R^+ + X{-}H \cdots A^-} \quad \text{(slow)} \tag{5}$$

$$\mathrm{R^+ + SOH \rightarrow R{-}O(H)S^+} \quad \text{(fast)} \tag{6}$$

$$\mathrm{R{-}O(H)S^+ + X{-}H \cdots A^- \rightarrow R{-}OS + X{-}H + A{-}H} \quad \text{(fast)} \tag{7}$$

The reaction of **1** in AcOH was monitored by GLC. The molar ratio AcOH : **1** required for convenient analysis (5 : 1) was such that pseudo-first-order kinetics could not be achieved. The earliest reaction products observed were 2,2-diacetoxypropane (**2**) and methanol. This result indicates that the solvolysis of the intermediate, 2-acetoxy-2-methyoxy-propane (**3**), by equation (9) is faster than its formation from **1** by equation (8). At longer reaction times, esterification of methanol with AcOH occurs (equation (10)) and the liberated water converts **2** to acetone and acetic acid (equation (11)), thus complicating the kinetics. The highest concentration of **2** in the mixture (ca. 10%) was observed at ca. 30% conversion of **1** (375 min). After two days of reaction, the reaction mixture consisted of acetone, methyl acetate, methanol, water, and acetic acid. The disappearance of **1** had a half-life of 825 min at 58 °C.

$$\mathrm{Me_2C(OMe)_2 + AcOH \rightarrow Me_2C(OMe)(OAc) + MeOH} \tag{8}$$

$$\mathrm{Me_2C(OMe)(OAc) + AcOH \rightarrow Me_2C(OAc)_2 + MeOH} \tag{9}$$

$$\mathrm{MeOH + AcOH \rightarrow AcOMe + H_2O} \tag{10}$$

$$\mathrm{Me_2C(OAc)_2 + H_2O \rightarrow Me_2C{=}O + 2AcOH} \tag{11}$$

When ketal **1** was heated in HFIP under the same conditions as in AcOH, no reaction whatsoever was observed even after 50 h, when the reaction in AcOH was essentially complete. This result demonstrated the total lack of activity of HFIP as an acid catalyst in this reaction.

In the next experiment, **1** was reacted in a mixture of AcOH and HFIP. The reaction was faster than in pure AcOH (half-life 730 min at 58 °C), even though the concentration of **1** was somewhat lower than in the run in neat AcOH and the concentration of the acid itself was reduced almost in half (cf. section 2). We had found earlier that addition of strong hydrogen bond donor solvents (anion-stabilizing solvents) increases the rates of carbocationic reactions in strongly acidic and weakly superacidic media [20]. We now find that the same effect is manifested on weak acids like AcOH. The reaction products at short and long reaction times were the same as in pure AcOH. No product or intermediate resulting from attack by HFIP was observed. The very low nucleophilicity of HFIP [21] could be responsible for this selectivity in the product-forming step (equation (6)). Alternatively, the product-forming step may involve recombination of the ion pair resulting from the rate-determining step (equation (5)).

Table 2
Hydrolysis of sucrose catalyzed by PMA.

Temp. (°C)	$10^4 k$ ($\mathrm{min^{-1}}$)	Activation parameters
63	1.92	$\Delta H^\ddagger = 8.62$ kcal/mol
68	2.54	$\Delta S^\ddagger = -58.2$ cal/mol °C
73	2.87	$E_\mathrm{a} = 9.3$ kcal/mol

The catalytic activity of the solids was tested for the hydrolysis of sucrose [22]. As expected, PMA possessed catalytic activity for that reaction. Maintaining the quantity of resin constant in all experiments, as described in section 2, we obtained the pseudo-first-order rate constants at three temperatures shown in table 2. Whereas the rate constants are in the same range as reported by previous investigators [22], the activation energy, also given in table 2, is much smaller, suggesting that the diffusion plays an important role for the polymer which we used. Note, however, that the temperature range of the experiments in table 2 is rather narrow.

When PMA was replaced in the experiment by the much better hydrogen bond donor silica gel, no reaction of sucrose was observed after two days of stirring at 68 °C. Note that silica gel had a much larger surface area than PMA. Also, there is no impediment to the access of reactant molecules to the strong hydrogen-bonding sites of silica gel. Indeed, reactions in solution catalyzed by dissolved acids, are accelerated upon addition of silica gel [23], showing that both the acid and the substrate are easily adsorbed onto the surface and the hydrogen bond donor ability of silica gel accelerates the reaction by anion stabilization [17,20,24]. The hydrogen bond donor ability does not reflect, however, any significant acidity of the solid. Thus, the solids exhibit the same lack of correlation of hydrogen bond donor ability with acid strength, measured by catalytic activity, as the liquids.

4. Conclusion

Our results demonstrate the absence of any correlation between the hydrogen bond donor ability of a molecule or material and its acid strength, measured either by a hydronation equilibrium or by the rate of an acid-catalyzed reaction, because weaker acids are sometimes better hydrogen bond donors than stronger acids. A direct correlation of acid strength with hydrogen bond donor ability is possible only when each group (acids and bases) involved in the comparison consists of very close structural relatives [11]. When such a correlation is found for a family of acids with a given hydrogen bond acceptor, it should not be used to predict acid strength or catalytic activity toward compounds of different structural type than the acceptor. A strong hydrogen bond donor enhances, however, the catalytic activity of an acid catalyst, in agreement with our previous findings [17,20].

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References

[1] (a) J.N. Brønsted and K. Pedersen, Z. Physik. Chem. 108 (1923) 185;
(b) M. Eigen, Angew. Chem. 75 (1963) 489.
[2] J.F. Bunnett and R.A.Y. Jones, Pure Appl. Chem. 60 (1988) 1115.
[3] D. Făcaşiu, A. Ghenciu and J.Q. Li, J. Catal. 158 (1996) 116.
[4] (a) H.A. Benesi and B.H.C. Winquist, in: *Advances in Catalysis*, Vol. 27, eds. D. Eley, H. Pines and P.B. Weisz (Academic Press, New York, 1978) p. 97;
(b) W.E. Farneth and R.J. Gorte, Chem. Rev. 95 (1995) 615;
(c) D. Fărcaşiu and A. Ghenciu, Progr. NMR Spectroscopy 29 (1996) 129.
[5] D. Fărcaşiu and D. Hâncu, J. Chem. Soc. Faraday Trans. 93 (1997) 2161.
[6] (a) H.S. Bloch, H. Pines and L. Schmerling, J. Am. Chem. Soc. 68 (1946) 153;
(b) C.D. Nenitzescu, M. Avram and E. Sliam, Bull. Soc. Chem. France (1955) 1266;
(c) J.M. Oelderik, cited in: D.M. Brouwer and E.L. Mackor, Proc. Chem. Soc. (1964) 147;
(d) J.M. Oelderik, E.L. Mackor, J.C. Platteeuw and A. van der Wiel, Brit. Patent 981311 (1962); see also US Patent 3201494 (1965);
(e) D.M. Brouwer and H. Hogeveen, Progr. Phys. Org. Chem. 9 (1972) 179.
[7] (a) H. Hogeveen and A.F. Bickel, Chem. Commun. 635 (1967);
(b) G.A. Olah and J. Lukas, J. Am. Chem. Soc. 89 (1967) 2227, 4739.
[8] G.A. Olah, G.K.S. Surya-Prakash and J. Sommer, *Superacids* (Wiley–Interscience, New York, 1985).
[9] M.M. Davis, *Acid–Base Behavior in Aprotic Organic Solvents*, NBS Monograph, Vol. 105 (National Bureau of Standards, Washington, DC, 1968).
[10] D. Fărcaşiu, J. Catal. 160 (1966) 309.
[11] (a) A. Zecchina, R. Buzzoni, S. Bordiga, F. Geobaldo, D. Scarano, G. Ricchiardi and G. Spoto, in: *Zeolites: A Refined Tool for Designing Catalytic Sites*, Proc. Int. Zeolite Symp., Quebec, 1995, eds. L. Bonneviot and S. Kaliaguine (Elsevier, Amsterdam 1995) p. 213;
(b) R. Buzzoni, S. Bordiga, G. Ricchiardi, C. Lamberti and A. Zecchina, Langmuir 12 (1996) 930;
(c) A. Zecchina, F. Geobaldo, G. Spoto, S. Bordiga, G. Ricchiardi, R. Buzzoni and G. Petrini, J. Phys. Chem. 100 (1996) 16584;
(d) A. Zecchina, S. Bordiga, G. Spoto, D. Scarano, G. Spano and F. Geobaldo, J. Chem. Soc. Faraday Trans. 92 (1996) 4863.
[12] (a) D. Fărcaşiu, J. Catal. 167 (1997) 303;
(b) D. Fărcaşiu and D. Hâncu, Abstr. P55 presented at the 15th Meeting of the North American Catal. Soc., Chicago, IL, 19 May 1997.
[13] (a) D. Fărcaşiu and A. Ghenciu, Catal. Lett. 31 (1995) 351;
(b) A. Ghenciu, Ph.D. thesis, University of Pittsburgh (1996).
[14] *Handbook of Chemistry and Physics*, 72nd Ed. (CRC Press, Boca Raton, FL, 1991) pp. 8–39.
[15] E.P. Parry, J. Catal. 2 (1963) 371.
[16] A.S. Tracey, B. Gallefi and S. Mahjour, Can. J. Chem. 66 (1988) 2294.
[17] D. Fărcaşiu, A. Ghenciu, G. Marino and K.D. Rose, J. Am. Chem. Soc. 119 (1997) 11826.
[18] F.A. Long and M.A. Paul, Chem. Rev. 57 (1957) 965.
[19] P.M. Leminger and M. Kilpatrick, J. Am. Chem. Soc. 60 (1938) 2891.
[20] D. Fărcaşiu, A. Ghenciu, G. Marino and R.V. Kastrup, J. Mol. Catal. 126 (1997) 141.
[21] D. Fărcaşiu, J. Jähme and C. Rüchardt, J. Am. Chem. Soc. 107 (1985) 5717, and references therein.
[22] G. Bodamer and R. Kunin, Ind. Eng. Chem. Int. Ed. 43 (1951) 1082.
[23] P.J. Kropp, K.A. Daus, S.D. Crawford, M.W. Tubergen, K.D. Kepler, S.L. Craig and V.P. Wilson, J. Am. Chem. Soc. 112 (1990) 7433, and subsequent papers.
[24] D. Fărcaşiu, in: *Nucleophilicity*, Advances in Chemistry Series, Vol. 215, eds. J.M. Harris and S.P. McManus (American Chemical Society, Washington, DC, 1987) chapter 20.