

Thermochemical Comparisons of Solid and Homogeneous Acids and Bases: Pyridine and Polyvinylpyridine as Prototype Bases

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Abstract: By means of a previously established thermochemical technique, the basic properties of polyvinylpyridine slurries in acetonitrile are compared with those of solutions of pyridine through their heats of interaction with a series of carboxylic and sulfonic acids. An excellent correlation between the heats of interaction obtained by titration calorimetry, ΔH_{titr} , for the homogeneous versus heterogeneous systems is obtained which is similar to that for a previous correlation of ΔH_{titr} for a series of bases into solutions of *p*-toluenesulfonic acid versus slurries of a microporous sulfonic acid resin. In both cases it appears that only the most available surface sites are being titrated since ΔH_{titr} values correlate poorly with corresponding heats of immersion. Important differences between homogeneous and solid acid-base systems are stressed and an inherent lack of symmetry between the nature of acid-base interactions at the surfaces of acidic and basic solids.

Introduction

Classification of compounds into acids or bases is one of the oldest and most useful in chemistry. Gas-phase comparisons of proton transfer, which have become available in recent years,¹⁻⁵ provide the broadest spectrum of structure-reactivity relationships for the transfer of protons or other acids⁶ and is of most immediate value for theoretical interpretations. In solution, acid-base chemistry has been of fundamental importance for determining both the nature and distribution of products since the vast majority of organic processes in solution occur through polar media involving nucleophilic or electrophilic attack by intermediates generated by the presence of bases or acids.

Quantitative treatment of acid-base catalysis was restricted for many years to the pH range in dilute aqueous solutions, but was extended rigorously over the entire range of aqueous acid solutions through the pioneering studies of Hammett and his co-workers,⁷ first as a means for describing acid-base equilibria rigorously and then to the interpretation of catalysis in strong aqueous acids and bases. Many subsequent studies⁸⁻¹¹ have established the acidity function method as a rigorous means for relating an enormous range of acids and bases to a common scale.

Since many industrial, geothermal, and biological processes take place at the interfaces of solids with liquids or gases, there has been a long-standing effort to relate the acid-base properties of solids to the more familiar and tractable ones of homogeneous solutions. To this end, the first major attempt by Walling¹² used

the color changes of a series of Hammett indicators as a means for calibrating the relative acidities of a variety of aluminas and aluminosilicates. Although there are numerous practical and theoretical difficulties in applying the Hammett acidity function to suspensions of solids in hydrocarbon media, the method has been developed carefully and is still the most widely used technique for comparing an enormous variety of solids which show acidic behavior.¹³⁻²⁰ Subsequently, the Hammett-Walling approach has been extended as a means for comparing the strengths of solid bases such as alkaline earth oxides and basic resins as well as acids and superacids.²¹

The Hammett acidity-basicity function method requires development of a linear free energy relationship for a series of structurally related indicator bases of overlapping base/acid strength. The difficulty of applying any such extrapolation to bases or acids of widely different structural types has led to the proliferation of a wide variety of acidity-basicity functions^{9,10,22} with the ultimate recognition that each compound has its own function and therefore cannot be fitted perfectly to any single scale developed from a series of other bases or acids.

Some years ago we demonstrated that an alternative thermochemical approach could be used which was applicable whether or not the compound had detectable indicator properties. This approach could be applied to solids as well as to homogeneous systems.²³ The method simply involves the injection or immersion

(1) Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol 2, pp 1-51 and references therein.

(2) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 3, 695-808.

(3) Taft, R. W. In *Progress in Physical Organic Chemistry*; John Wiley: New York, 1983; Vol. 14, pp 247-350.

(4) Arnett, E. M. *Acc. Chem. Res.* **1973**, *6*, 404.

(5) Epshtein, L. M. *Russ. Chem. Rev.* **1979**, *48* (9), 854.

(6) (a) Brown, H. C.; McDaniel, D. H.; Häfliger, O. In *Determination of Organic Structures by Physical Methods*; Braude, E. A., Nachod, F. C., Eds.; Academic Press: New York, 1955; pp 567-652 and references therein. (b) Brown, H. C. *J. Chem. Soc.* **1956**, 1248-68 and references therein.

(7) (a) Hammett, L. P.; Deyrup, A. J. *J. Am. Chem. Soc.* **1932**, *54*, 2721. (b) Hammett, L. P.; Paul, M. A. *J. Am. Chem. Soc.* **1934**, *56*, 527.

(8) Rochester, C. H. *Acidity Functions*; Academic Press: New York, 1970.

(9) Arnett, E. M. *Progress in Physical Organic Chemistry*; John Wiley: New York, 1963; Vol. 1, pp 223-403.

(10) (a) Cox, A. R.; Yates, K. *J. Am. Chem. Soc.* **1978**, *100*, 3861. (b) Cox, A. R.; Yates, K. *Can. J. Chem.* **1981**, *59*, 2116. (c) Cox, A. R.; Yates, K. *Can. J. Chem.* **1983**, *61*, 2225.

(11) Olah, G. A.; Prakash, G. K. S.; Sommer, J. In *Superacids*; John Wiley: New York, 1985.

(12) Walling, C. J. *Am. Chem. Soc.* **1950**, *72*, 1164.

(13) (a) Benesi, H. A. *J. Am. Chem. Soc.* **1956**, *78*, 5490. (b) Benesi, H. A. *J. Phys. Chem.* **1957**, *61*, 970.

(14) Forni, L. *Catal. Rev.* **1973**, *8* (1), 65-115.

(15) Jacobs, P. A. In *Characterization of Heterogeneous Catalysts*; Delannay, F., Ed.; Marcel Dekker: New York-Basel, 1984; Vol. 15, pp 367-404.

(16) Rys, P.; Steinegger, W. *J. Am. Chem. Soc.* **1979**, *101*, 4801.

(17) Atkinson, D.; Curthoys, G. *Chem. Soc. Rev.* **1979**, *8*, 475.

(18) Ferry, L. L. *J. Macromol. Sci.-Chem.* **1990**, *A27*, (8), 1095.

(19) (a) Mishima, S.; Nakajima, T. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1307. (b) Mishima, S.; Matsuzaki, I.; Nakajima, T. *J. Chem. Soc., Faraday Trans.* **1990**, *86* (20), 3447.

(20) For a careful critique of some of the above methods of catalyst characterization, see: Deeba, M.; Hall, W. K. *J. Catal.* **1979**, *60*, 417; *Z. Phys. Chem. (Frankfurt am Main)* **1985**, *144*, 85.

(21) (a) Tanabe, K. In *Solid Acids and Bases*; Academic Press: New York, London, 1970; Chapter 5. (b) Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. In *New Solid Acids and Bases. Studies in Surface Science and Catalysis*; Delmon, B., Yates, J. T., Advisory Eds.; Elsevier: Amsterdam-Oxford-New York-Tokyo, 1989; Vol. 51.

(22) (a) Arnett, E. M.; Mach, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 1177.

(b) Bollinger, J. M.; Burke, J. J.; Arnett, E. M. *J. Org. Chem.* **1966**, *31*, 1310.

(23) (a) Arnett, E. M.; Burke, J. J. *J. Am. Chem. Soc.* **1966**, *88*, 4308.

(b) Arnett, E. M.; Quirk, R. P.; Burke, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 1260. (c) Arnett, E. M.; Quirk, R. P.; Larsen, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 3977. (d) Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875.

Table I. Heats of Interaction of Some Strong Acids 0.25 M in Acetonitrile with Poly-4-vinylpyridine (PVP) and Pyridine at 25 °C

no.	acid	pK_a	$-\Delta H_{\text{titr}}$ (kcal mol ⁻¹)		$-\Delta H_{\text{imm}}$ (cal g ⁻¹)
			PVP	pyridine	PVP
1.	4-toluenesulfonic	-6.55 ^a	16.56 ± 0.46	15.24 ± 0.27	66.89 ± 1.99
2.	benzenesulfonic	-2.70 ^a	17.35 ± 0.34	16.61 ± 0.17	62.08 ± 0.53
3.	methanesulfonic	-1.92 ^b	15.49 ± 0.24	14.70 ± 0.19	147.55 ± 1.25
4.	ethanesulfonic	-1.68 ^b	14.65 ± 0.17	14.11 ± 0.22	148.33 ± 17.0
5.	4-nitrobenzenesulfonic	-4.00 ^a	11.31 ± 0.46 ^c	10.32 ± 0.23 ^c	
6.	4-chlorobenzenesulfonic		15.91 ± 0.25	14.45 ± 0.23 ^c	53.26 ± 1.37
7.	trichloroacetic	0.69 ^d	11.28 ± 0.12	10.52 ± 0.18	80.82 ± 1.40
8.	trifluoroacetic	0.54 ^d	11.20 ± 0.24	10.61 ± 0.10	85.75 ± 0.72
9.	dichloroacetic	1.36 ^d	7.63 ± 0.11	7.25 ± 0.05	70.56 ± 0.82
10.	difluoroacetic	1.30 ^d	6.75 ± 0.19	6.96 ± 0.19 ^c	74.99 ± 1.89
11.	cyanoacetic		3.64 ± 0.06 ^c	4.69 ± 0.08 ^c	55.86 ± 2.39
12.	trifluoromethanesulfonic		24.80 ± 0.43 ^c	23.08 ± 1.37 ^c	130.39 ± 9.45
13.	boron trichloride ^e		60.65 ± 0.92 ^c	58.60 ± 4.62 ^c	

^a From ref 36. ^b From ref 37. ^c Average of one set of runs. ^d From ref 38. ^e Hexane as solvent; these results were not reproducible when different batches of BCl₃ were used on different days. Discrepancies as large as 30 kcal mol⁻¹ were obtained.

of the acidic or basic liquid or solid into a solution of strong base or strong acid in a calorimeter and measuring the heat generated. By this method the heats of ionization of some 50 compounds of widely varied base strength were determined in pure sulfuric acid and were shown to correlate closely with their pK_a s referred to the usual standard state of high dilution in water on which all acidity functions in aqueous acid are referred. A complementary study used KDMSYL in DMSO as a superbases system for deprotonating a variety of acids.²⁴

Recently, we have applied the above approach as a means for comparing the acidity of suspensions of sulfonic acid resins in nonaqueous solvents to that of equivalent solutions of *p*-toluenesulfonic acid against strong Brønsted bases.²⁵ An excellent correlation was found between the heats of interaction of 29 nitrogen bases with the two different acidic systems, providing support for the use of sulfonic acid resins as prototype standards for comparison of solid Brønsted acids. The same method was applied to correlating the heats of interaction of the same bases with silicas²⁶ and solutions of *p*-fluorophenol as prototype hydrogen-bonding systems and later to aluminas²⁷ and graphitized carbon black²⁸ (as a dispersion force model), and finally to a variety of coals²⁹ as examples of complex acidic behavior.

The present article now approaches the comparison of homogeneous and heterogeneous bases through the heats of interaction of a series of carboxylic and sulfonic acids with solutions of pyridine and suspensions of polyvinylpyridine (PVP) as prototypes for comparing homogeneous and heterogeneous bases.

Experimental Section

The same techniques were used as described previously.²⁵ The polymeric resin (poly-4-vinylpyridine) was obtained from Reilly Chemicals and was dried in a vacuum oven at 80 °C for about 50 h prior to the titrametric studies. The dried polymer was stored in a Vacuum Atmospheres drybox under argon throughout the course of the experimental work. All the acids were obtained from Aldrich and were used as solutions in anhydrous acetonitrile. The boron trichloride was obtained as 1 M solution in hexane from Aldrich. The medium for reaction calorimetry with this acid and for its dilution was anhydrous hexane. The pyridine was distilled under argon after stirring with KOH pellets for about 1.5 h. The distillate was collected at 114 °C and stored in a dessicator.

The heats of reaction of pyridine and the polymeric resin (as a slurry in acetonitrile) with the acid solutions (0.1–0.3 M) at 25 °C were mea-

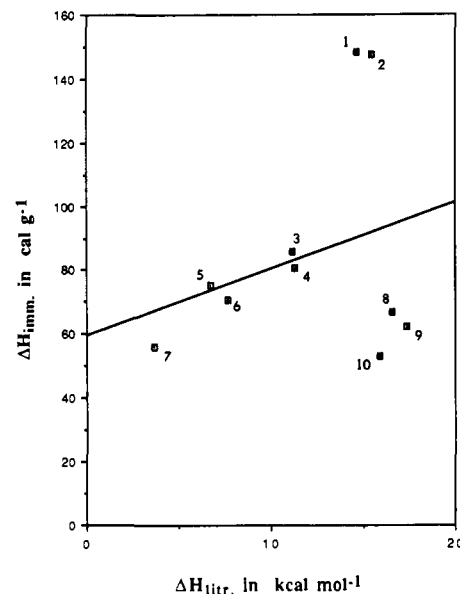


Figure 1. Plot of ΔH_{imm} versus ΔH_{titr} for poly-4-vinylpyridine in various acids at 25 °C: (1) ethanesulfonic acid, (2) methanesulfonic acid, (3) trifluoroacetic acid, (4) trichloroacetic acid, (5) difluoroacetic acid, (6) dichloroacetic acid, (7) cyanoacetic acid, (8) 4-toluenesulfonic acid, (9) benzenesulfonic acid, (10) 4-chlorobenzenesulfonic acid.

sured by thermometric titrations using a Tronac 450 titration calorimeter. The calorimeter was calibrated by measuring the heats of reaction of aqueous NaOH and HCl solutions. The values obtained (-13.42 ± 0.39 kcal mol⁻¹) agreed well with the standard published values.³⁰

The heat of immersion experiments were carried out using the Setaram C-80 heat flow microcalorimeter which operates on the Tian-Calvet heat-flow principle.³¹ It was operated as described previously.²⁶ The instrument was calibrated by measuring the heats of dissolution of dry KCl in water at 25 °C; the values obtained (4.098 ± 0.035 kcal mol⁻¹) agreed well with the standard value.³²

Results

Table I presents heats of interaction of pyridine and PVP with carboxylic and sulfonic acids at 25 °C in acetonitrile. ΔH_{titr} values were obtained by titration calorimetry. The acid solution was pumped at a constant speed into a calorimeter containing the well-stirred solution or suspension of the base. In contrast ΔH_{imm} refers to heat of immersion experiments in which the solid base is suddenly released into a solution of the acid. Since it is known exactly how many moles of acid react with a large excess of base,

(24) (a) Arnett, E. M.; Moriarity, T. C.; Small, L. E.; Rudolph, J. P.; Quirk, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 1492. (b) Arnett, E. M.; Venkatsubramaniam, K. G. *J. Org. Chem.* **1983**, *48*, 1569.

(25) Arnett, E. M.; Haaksma, R. A.; Chawla, B.; Healy, M. H. *J. Am. Chem. Soc.* **1986**, *108*, 4888.

(26) Arnett, E. M.; Cassidy, K. F. *Rev. Chem. Intermed.* **1988**, *9*, 27.

(27) Healy, M. H.; Wiserman, L. F.; Arnett, E. M.; Wefers, K. *Langmuir* **1989**, *5*, 114.

(28) Arnett, E. M.; Hutchinson, B. J.; Healy, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 5255.

(29) (a) Chawla, B.; Arnett, E. M. *J. Org. Chem.* **1984**, *49*, 3054. (b) Arnett, E. M.; Liu, Q.; Gumkowski, M. *Energy Fuels* **1988**, *2*, 295.

(30) Tyson, B. C., Jr.; McCurdy, W. H., Jr.; Bricker, C. E. *Anal. Chem.* **1961**, *33*, 1640.

(31) Calvet, E. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956.

(32) *Handbook of Chemistry and Physics*, 70th ed.; CRC Press: Boca Raton, FL, 1989–90; pp D-122.

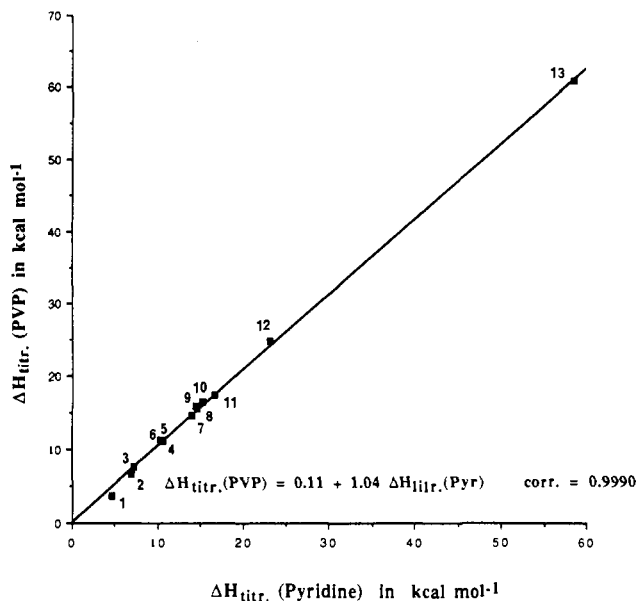


Figure 2. Correlation for ΔH_{titr} of acids with excess pyridine and poly-4-vinylpyridine resin in acetonitrile at 25 °C: (1) cyanoacetic acid, (2) difluoroacetic acid, (3) dichloroacetic acid, (4) trifluoroacetic acid, (5) trichloroacetic acid; (6) 4-nitrobenzenesulfonic acid, (7) ethanesulfonic acid; (8) methanesulfonic acid; (9) 4-chlorobenzenesulfonic acid; (10) 4-toluenesulfonic acid; (11) benzenesulfonic acid; (12) trifluoromethanesulfonic acid, (13) boron trichloride (hexane solvent).

ΔH_{titr} can be expressed in kcal mol⁻¹. For heats of immersion, all that is known is the weight of base suddenly added to the excess acid, and there is no means of knowing exactly how many moles of acid or base are involved in the reaction; accordingly, the units are cal g⁻¹.

In order to observe a Lewis acid interaction with both pyridine and the PVP slurries, we used BCl₃ solution in hexane. The reported data for this acid in Table I were very irreproducible, because of the difficulty involved in controlling the absolute concentration of BCl₃ in hexane since both are highly volatile! Although we could not determine accurate reproducible values for the heat data, ΔH_{titr} for reaction of the homogeneous and heterogeneous bases that were taken sequentially within a short period of time agreed closely with each other. However, the results were wildly different if repeated on different days with different batches of BCl₃ solution.

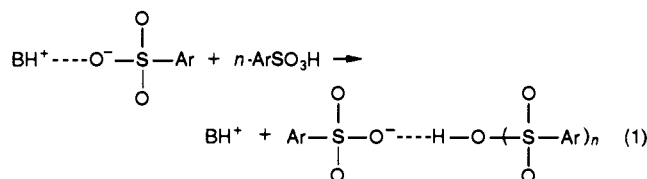
Although the ΔH_{titr} for PVP and pyridine follow parallel trends (see below) with each other and with pK_as, there are sharp differences between the order of ΔH_{titr} for PVP and the corresponding ΔH_{imm} . In contrast, as Figure 1 demonstrates dramatically, there is no correlation between heats of immersion and titrimetric heats for polyvinylpyridine. In a previous comparison of ΔH_{titr} and ΔH_{imm} for silicas in a series of bases, only a poor correlation was obtained between the two methods. In the present case the difficulty appears to be the result of a slow chemical attack of methane- and ethanesulfonic acid on polyvinylpyridine following the initial fast exothermic interaction. The difference in behavior of the halogenated aliphatic acids and the aliphatic sulfonic acids probably reflects a difference between their corresponding interactions with the solid base. The aliphatic acetic acids seem to interact with the accessible basic sites only, whereas the aliphatic sulfonic acids after reacting with the surface sites penetrate the polymer matrix with slow evolution of heat. The magnitude of ΔH_{imm} for methane- and ethanesulfonic acid supports this interpretation. The aryl sulfonic acids on the above-mentioned plot are grouped together at a common level separated from the aliphatic correlation line. Their position appears to reflect the difficulty involved in their approach to the less accessible sites on the polymer in ΔH_{imm} experiments.

Discussion

The most significant feature of this investigation is the excellent correlation shown in Figure 2 between the titrimetric heats of

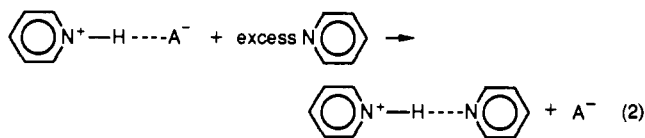
interaction, for the whole series of acids with solutions of pyridine, and suspensions of polyvinylpyridine. This provides strong evidence that the ionization processes which occur at the most accessible surface sites on the PVP particles are modeled exactly by the corresponding ionization of free pyridine molecules upon interaction with the various acids in this study.

Figure 2 corresponds for solid bases to the equivalent correlation in our previous report²⁵ for the titrimetric heats of interaction of a series of bases with *p*-toluenesulfonic acid and Dowex sulfonic acid resin. Both cases demonstrate that under favorable circumstances there is little inherent difference between a Brønsted acid-base interaction at a readily accessible solid surface as compared to that which occurs in solution. However, Figure 2 provides an interesting contrast to the previous correlation for a series of bases with homogeneous and heterogeneous sulfonic acid systems. Although in both cases good linear correlations are found with *R* greater than 0.995, and with slopes close to unity, ΔH_{titr} values for the bases with solutions of *p*-toluenesulfonic acid were on the average nearly 5 kcal mol⁻¹ more exothermic than for the corresponding interactions on the surface of the sulfonic acid resin. This was attributed to a strong homo-hydrogen-bonding interaction between excess sulfonic acid molecules in solution which readily displace the ammonium ion from its hydrogen-bonded ion pair



with the aryl sulfonate anion in solution but which are prevented by steric restrictions on the sulfonic acid groups distributed and relatively immobilized within the structure of the resin. This type of homo-hydrogen-bonding interaction should depend upon the degree of sulfonation, cross-linking, and the amount of swelling, as well as the surface area of the resin.^{33,34}

Arguments in favor of the homo-hydrogen-bonding explanation were provided by the variation of the acid-base ratio and reverse addition experiments. These showed that in the absence of the large excess of free sulfonic acid in solution there was little difference between the heat of interaction between pyridine with the homogeneous as compared to the heterogeneous system. It is gratifying to see that the value 15.24 ± 0.27 in Table I for the titration of *p*-toluenesulfonic acid solution into excess pyridine solution is close to the limiting value²⁵ reported in the previous study as the acid to base ratio was gradually reduced to the 1:1 equivalent level and that was obtained by direct titration of PTSA into pyridine as in the present report. From the above discussion it appears that the nearly zero intercept in Figure 2 implies a much weaker interaction between excess pyridine and pyridinium ions to displace the carboxylate or sulfonate counterion (eq 2) than



between sulfonic acids with sulfonate anions (eq 1). Note that in this case only one py⁺-H-py bond³⁵ can be formed, whereas three hydrogen bonds could form from excess sulfonic acid molecules to each sulfonate anion.³⁴

(33) (a) Buttersack C.; Widdecke, H.; Klein, J. *J. Mol. Catal.* **1986**, *35*, 77. (b) Buttersack, C.; Widdecke, H.; Klein, J. *Reactive Polymers* **1987**, *5*, 181. (c) Buttersack, C. *Reactive Polymers* **1989**, *10*, 143.

(34) Zundel, G. *Hydration and Intermolecular Interaction—Infrared Investigations with Polyelectrolyte Membranes*; Academic Press: New York, 1969.

(35) (a) Davis, M. M. *Acid-Base Behavior in Aprotic Organic Solvents*; National Bureau of Standards Monograph No. 105; National Bureau of Standards: Washington, DC, 1968. (b) Davis, M. M. In *The Chemistry of Non-Aqueous Solvents*; Lagowski, J. J., Ed.; Academic Press: New York-London, 1970; Vol. 3, pp 1-135.

It is widely recognized that, in general, acid-base chemistry on solid surfaces may be fundamentally different from that in solution because of the spatial arrangement of sites of drastically different types and strengths of acidities. In a well-stirred solution any distribution of Brønsted, hydrogen bonding, and Lewis acid sites comes almost instantly to an equilibrium in which the standard free energy of interaction of a base with any type of site must be equivalent to the other. In contrast, the surface of a solid acid may have Lewis, Brønsted, and hydrogen-bonding sites of widely varied strengths which are permanently separated so that there is no feasible means for them to reach an equilibrium. Many ingenious techniques have been developed for obtaining the distribution of different types of acid sites on complex solid acids including the thermometric method described above.

Finally, it is important to point out a fundamental difference between the behavior of solid acids and solid bases. There are

three clearly defined types of acids (Lewis, Brønsted, and hydrogen-bond donor) which show different patterns of interaction with bases.^{2,3d} However, there is ultimately only one type of basic site, namely, the electron pair, although that is surely modulated by the type of atom to which it is attached and its environment both inter- and intramolecular. The present study has focused deliberately on a simple type of interaction of strong Brønsted acids with a clearly defined type of basic resin for which there is a simple homogeneous model. In subsequent studies we expect to compare these results with those for the interaction of other solid bases with hydrogen-bonding, Lewis and Brønsted.

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Registry No. PVP, 9003-47-8; 4-toluenesulfonic acid, 104-15-4; benzenesulfonic acid, 98-11-3; methanesulfonic acid, 75-75-2; ethanesulfonic acid, 594-45-6; 4-nitrobenzenesulfonic acid, 138-42-1; 4-chlorobenzenesulfonic acid, 98-66-8; trichloroacetic acid, 76-03-9; trifluoroacetic acid, 76-05-1; dichloroacetic acid, 79-43-6; difluoroacetic acid, 381-73-7; cyanoacetic acid, 372-09-8; trifluoromethanesulfonic acid, 1493-13-6; boron trichloride, 10294-34-5; pyridine, 110-86-1.

(36) Guthrie, J. P. *Can. J. Chem.* 1978, 56, 2342.

(37) Gurnine, S. D.; Shankweiler, J. M.; Hoffman, R. V. *J. Org. Chem.* 1986, 51, 25, 5013.

(38) Shelly, K. P.; Venimadhavan, S.; Nagarajan, K.; Stewart, R. *Can. J. Chem.* 1989, 67, 1274.

Heats of Interaction of Strong Brønsted Acids with Silica

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Abstract: Heats of immersion (ΔH_{imm}) are reported for a well-characterized commercial silica into acetonitrile solutions of a series of strong protonic acids at 25 °C. Although the acids are of widely varying strength and might be expected to protonate the surface hydroxyl groups of the silica, or at least donate strong hydrogen bonds to them, there is only a modest variation in ΔH_{imm} . Significantly, all of the ΔH_{imm} values are less exothermic than the heat of immersion of the silica into neat acetonitrile, a poor hydrogen-bond donor but a moderately good acceptor. These surprising results are interpreted to mean that the various acids, both carboxylic and sulfonic, are actually behaving as hydrogen-bond acceptors from the surface of the silica on which cooperative hydrogen bonding between siloxy groups enhances the hydrogen-bonding donor ability of the surface sites. This interpretation is supported by FTIR examination of the surface, and by demonstration that the heat of immersion of the silica in dichloroacetic acid decreases steadily as the density of hydrogen-bonded silanols is reduced by high-temperature activation.

Introduction

Although the majority of ordinary laboratory operations occur in homogeneous liquid media, many industrial, geochemical, and chromatographic operations occur at the interface between solid surfaces and liquids or gases. Many reactions occurring at solid surfaces give ample evidence of being promoted by the acidic or basic properties of the solid surface.¹ Accordingly, there has been a strong incentive for developing methods by which the acid-base properties of solids might be related to the well-established thermodynamic scales for comparing the abilities of organic compounds to give or accept protons, hydrogen bonds, or coordinate covalencies both in the gas phase and in solution. These methods have been reviewed repeatedly.²

Five years ago we initiated a thermochemical study which aimed to compare carefully chosen solid acids with their homogeneous analogues.³ An excellent correlation was found between the heats

of reaction of 29 nitrogen bases with suspensions of a microporous polymeric aryl sulfonic acid resin (Dowex W-X8) in acetonitrile versus corresponding heats of ionization of the same bases by *p*-toluenesulfonic acid in the same solvent. Following this success it was demonstrated through a variety of experiments that there was an acceptable correlation between heats of interaction of a variety of bases with several kinds of silica and the corresponding heats of hydrogen-bond formation between the same bases and *p*-fluorophenol.⁴ Subsequently, it was shown that heats of adsorption of a wide variety of compounds on several kinds of graphitized carbon black had no relation at all to the acid-base properties of the adsorbates, but were correlated well with their total polarizabilities.⁵ With these data in hand as models for solid Brønsted acids (the sulfonic acid resin) and solid hydrogen-bond donors (silica), and graphitized carbon as a model for adsorption by dispersion force interactions, the heats of adsorption of a number of bases on a variety of well-characterized coal samples were analyzed by multiparameter statistical correlations in terms

(1) Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. In *New Solid Acids and Bases, Studies in Surface Science and Catalysis*; Delmon, B., Yates, J. T., Advisory Eds.; Elsevier: New York, 1989; Vol 51 and references therein.

(2) (a) Forni, L. *Catal. Rev.* 1973, 8 (1), 65-115. (b) Atkinson, D.; Curthoys, G. *Chem. Soc. Rev.* 1979, 8, 475. (c) Jacobs, P. A. In *Characterization of Heterogeneous Catalysts*; Delannay, F., Ed.; Marcel Dekker: New York-Basel, 1984; Vol. 15, pp 367-404.

(3) Arnett, E. M.; Haaksma, R. A.; Chawla, B.; Healy, M. H. *J. Am. Chem. Soc.* 1986, 108, 4888.

(4) Arnett, E. M.; Cassidy, K. F. *Rev. Chem. Intermed.* 1988, 9, 27.

(5) Arnett, E. M.; Hutchinson, B. J.; Healy, M. H. *J. Am. Chem. Soc.* 1988, 110, 5255.