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.[23d] 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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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

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Table I. Heats of Immersion (ΔH_{imm}) of Fisher Silica in Some Solutions of Acids and Bases (1 M in Acetonitrile, at 25 °C) and in Pure Nitrogen Bases from Previous Study

acids	$-\Delta H_{imm}$ (cal/g)	ΔH_{imm} in H_2SO_4 (kcal mol^{-1})	bases[a]	ΔH_{imm} (cal/g of silica)
hexane (neat)	3.81 ± 0.00		cyclohexanone	18.41 ± 1.08
ethyl acetate (neat)	15.78 ± 2.88		3,5-dichloropyridine	18.87 ± 1.04
difluoroacetic	16.41 ± 0.20	1.28	acetonitrile	19.82 ± 0.52
4-chlorobenzenesulfonic	17.08 ± 0.16		2,4,6-trimethylpyridine	21.89 ± 0.70
4-toluenesulfonic	17.12 ± 0.26		3-bromopyridine	22.96 ± 0.39
benzenesulfonic	17.26 ± 0.11		4-methylpyridine	23.02 ± 0.52
trichloroacetic	17.53 ± 0.91		2,6-dimethylpyridine	23.50 ± 1.04
ethanesulfonic	17.65 ± 0.66	1.90	diisopropylamine	24.00 ± 1.44
cyanoacetic	17.73 ± 0.20		triethylamine	24.44 ± 1.71
water (neat)	18.09 ± 1.04		pyridine	24.95 ± 0.48
dichloroacetic	18.12 ± 0.49 (17.83 ± 0.08)[b]	0.34	3-methylpyridine	25.11 ± 0.50
trifluoroacetic	18.90 ± 1.14 (15.61 ± 0.41)[b]	0.17	2-methylpyridine	26.34 ± 0.75
methanesulfonic	20.25 ± 0.09 (17.55)[b]	1.24		
water	20.41			
chloroacetic	20.41 ± 0.28			
acetic	19.65 ± 0.38 (16.97 ± 1.25)[b]	8.34		
acetonitrile (neat)	21.41 ± 1.00			
ethyl acetate	21.75			

[a] From ref 4.   [b] Hexane as solvent.

of Brønsted acid, hydrogen bonding, and dispersion force interactions.[6]

We now attempt to investigate the other half of the solid acid–base problem by determining the heats of interaction for a series of acids of varied strength with appropriate solid bases. The preceding article[7] reports our comparison of the heats of interaction for a series of acids with slurries of polyvinylpyridine and with solutions of pyridine in acetonitrile. This report describes our attempt to study silica as a solid acceptor of protons or of hydrogen bonds from the same series of protonic acids.

Of all solid surfaces, that of silica is probably the least complicated, most readily variable, and most widely characterized.[8a-c] In spite of this, there is controversy[8d,e] regarding the heterogeneous nature of the silica surface. This heterogeneity arises partly from the processes involved during its precipitation (e.g., washing, drying, and the presence of metal impurities even at trace levels) and also from the thermal treatment. The thermochemical technique for comparing acid–base interactions[9] is especially versatile since it can be applied equally well to homogeneous and heterogeneous systems without regard to the thermodynamic assumptions which are required for the use of acidity functions, or the spectrophotometric requirements of indicator methods.[10] In view of the amphiprotic character of the hydroxyl function, it seemed a straightforward matter to examine the basicities of silica samples simply by determining their heats of interaction with a series of strong acids[11] in exactly the manner we had

employed previously for studying silicas as hydrogen-bonding acids against a series of nitrogen and oxygen bases. As will be seen below, the results instead testify to the powerful hydrogen-bond acidity of the silica surface and its low basicity even toward strong Brønsted acids.

Experimental Section

The same techniques were used as before[4] without modification. The silica was of ACS reagent grade (60–200 mesh, Lot 712393) used as received from Fisher Scientific Co. The specific surface areas were obtained by the BET method using a Quantachrome surface area analyzer. High-purity nitrogen was used in helium as an adsorbing gas. The silica samples were outgassed at 150 °C or at elevated temperatures in a vacuum oven for a period of 14–16 h prior to the heat of immersion studies. The acids were obtained commercially and were used as 0.25–0.50 M solutions in carefully purified acetonitrile or n-hexane or as neat liquids wherever indicated.

The heat of immersion studies on silica samples at 25 °C in solutions of acids or the neat liquid acids were made by using the Setaram C-80 differential microcalorimeter, which operates on the Tian-Calvet heat-flow principle. The calorimeter was calibrated periodically by measuring the heats of dissolution of KCl in water at 25 °C, and the values obtained (4.098 ± 0.035 kcal mol^{-1}) agreed well with the published value, 4.115 kcal mol^{-1}.[14] In immersion calorimetry in contrast to titration calorimetry (used in some previous studies), heat changes are expressed in cal g^{-1} rather than kcal mol^{-1} since the interaction with the solid is usually slow and it is not known how many sites, or of what kind, have reacted when a specified amount of silica is immersed into a large excess of acid. The heat was released gradually over a period of 30–40 min, but no long-term (1–2 h) heat evolution was observed.

Infrared spectra of thermally treated silica samples were obtained using a Nicolet IR 42 FTIR spectrometer (equipped with a photoacoustic detector and an MTEC Model 100 photoacoustic cell) at a scanning rate of 0.31 cm s^{-1}. Helium was used as a carrier gas in the photoacoustic cell because of its superior thermal coupling properties. All the spectra were standardized against that of carbon black powder. An IBM PC/AT computer was used for data acquisition and subsequent analyses.

Results and Discussion

Previously silica was chosen as a prototype solid hydrogen-bonding acid, and its heats of interaction with a series of bases correlated fairly well with their known heats of complexation with p-fluorophenol, a standard solution-phase hydrogen-bonding acid.[15] Since the silica hydroxyl groups are the hydrogen-bond donors and hydroxyl functions are amphiprotic, it is reasonable to expect that silica could also accept hydrogen bonds from sufficiently strong acids and perhaps even be protonated by them.[11] Accordingly, we began a series of experiments, the results of which

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(11) A referee has pointed out that silanol groups are usually considered to be weakly acidic, comparable to methanol. Aliphatic alcohols as acids have pK_as in the 17 to 20 range,[12] and as bases their pK_{BH^+}s lie from -2 to -5.[12] The H_0 of pure methanesulfonic acid is -7.86[13] which is more than adequate to protonate alcohols and, by analogy, silanols. **Note Added in Proof**: However, a recent gas-phase study (Damrauer, R.; Simon, S.; Krempp, M. *J. Am. Chem. Soc.* **1991**, *113*, 4431) reports that SiH$_3$OH is a stronger acid by 22 kcal/mol than CH$_3$OH.

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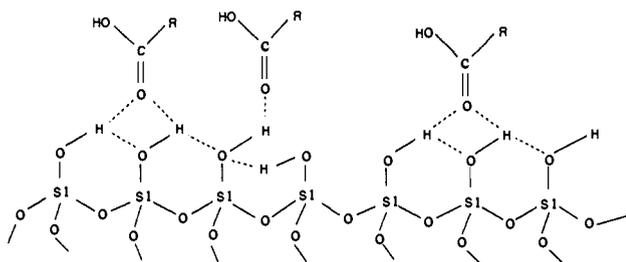
ΔH_{imm} of Strong Brønsted Acids with Silica

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Figure 1. Possible hydrogen-bonding interaction sites of the silica hydroxyl groups with the carbonyl groups of the acids.

are presented in Table I, to explore the interaction of a series of strong acids with a sample of Fisher silica whose surface properties we had examined and reported in our previous study.[4] In our opinion, the results in Table I suggest that silica is not acting as a base toward these strong acids, but is acting as a hydrogen-bonding acid toward them.

Surprisingly, the most exothermic heat of interaction for the whole series is for pure acetonitrile undiluted by any of the other materials. Acetonitrile is a very weak acid both in the Brønsted sense and also as a hydrogen-bond donor.[16] It is also a very weak Brønsted base since it is only partially protonated in pure sulfuric acid.[17] However (and this is probably the key to the strange order in Table I), it is a fairly good hydrogen-bond acceptor.[18] The principal fact that stands out from Table I is that, except for the understandably low heat of immersion of silica in pure hexane, all of the numbers are practically the same, lying in a very short range between 16.41 cal g^{-1} for difluoroacetic acid and 21.41 cal g^{-1} for pure acetonitrile. Significantly, ethyl acetate, which should be similar to acetic acid as a base, but which obviously cannot act as a strong protonic acid, lies in the same range as the other compounds.

Comparison with the heats of immersion of silica in the series of bases listed in the last column of Table I (from our previous study) suggests that the two sets of data have much in common. These are undoubtedly better hydrogen-bond acceptors than acetonitrile or the acids. These ΔH_{imm}s are more exothermic than those for silica in the acids but are still in the same range.

The present ΔH_{imm} for silica in acetonitrile is more exothermic by 1.59 cal g^{-1} than that obtained years ago in the previous study with the same batch of silica.[4] This difference is slightly outside the combined experimental error and, if it really is significant, may be due to traces of water in the previous solvent or a greater degree of hydration of the silica surface.

Our present interpretation of these results is that the principal contribution to all of these thermochemical values is from the interaction of silica as a hydrogen-bond donor with acetonitrile as acceptor. If this is true, the acids are simply serving as weakly basic diluents in the acetonitrile. Under these conditions *they are not acting as acids at all toward silica.*

That there can be a strong exothermic interaction between these acids and silica in the absence of acetonitrile is shown by the four starred numbers obtained with hexane solutions of methanesulfonic (sparingly soluble in hexane), trifluoroacetic, dichloroacetic, and acetic acids. Although there is no clear pattern, it is interesting that the interaction of silica with acetic acid is more exothermic than that with trifluoroacetic acid, although the latter is a much stronger acid and is a much weaker base[19] (see below). These four examples when taken against the background of the corresponding measurements in acetonitrile give strong support to the idea that in weakly basic solvents *these very strong acids are acting as hydrogen-bond acceptors rather than as proton donors or*

Table II. Variation of BET Surface Area to Fisher Silica with Activation Temperature

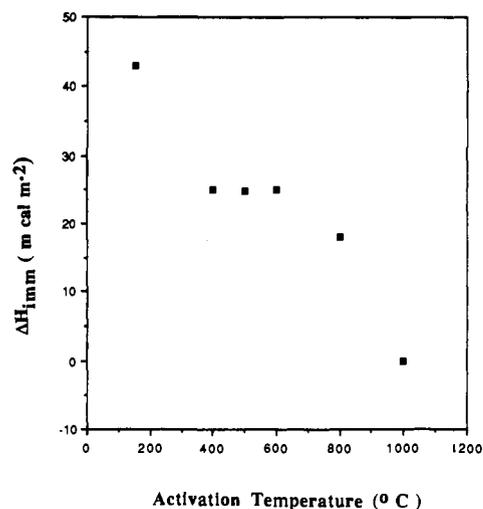| activation temp (°C)	surface area (m^2 g^{-1})	activation temp (°C)	surface area (m^2 g^{-1})
150	413.0 ± 7	600	322.7
400	428.1	800	329.8
500	429.9	1000	N/D

Figure 2. Variation of heats of immersion of Fisher silica in dichloroacetic acid with the activation temperature.

hydrogen-bond donors to the oxygens of silica.

Previous studies of carboxylic acids in aqueous strong acid solutions establish that protonation occurs on carbonyl oxygen.[20] Table I presents their ΔH_{imm}s in 98% H_2SO_4 which provides a crude comparison of the *basicities* of the acids shown.

Although there is a considerable literature[21-23] on the behavior of silica as a hydrogen-bond donor and its interaction with bases, we have found no published precedents for its interactions with strong acids that are directly relevant to the present case.

We propose that hydrogen bonding to the carbonyl oxygen of the carboxylic acids or to the sulfonic oxygens takes place from silica hydroxyl groups whose acidity is enhanced by cooperative hydrogen bonding at the surface; for example, see Figure 1.

This draws attention to the hydrogen-bond acceptor character of the carboxylate carbonyl group as being essentially that of a hydroxy ketone. In contrast, as a hydrogen-bond donor a carboxylic acid is like a keto alcohol R-C(=O)-OH--:B which does not enjoy the driving force for complete proton transfer to produce a resonance-stabilized carboxylate anion.

In order to probe the above hypothesis a sample of silica was activated at a series of elevated temperatures ranging from 150 °C to 1000 °C before measuring its heats of immersion in a 0.75 M solution of dichloroacetic acid in hexane. The BET-nitrogen surface area data for the silica after activating at various temperatures are given in Table II. The surface area remains nearly constant (413–430 m^2 g^{-1}) to activation at temperatures up to 500 °C but decreases markedly at higher temperatures ($\approx$322–329 m^2 g^{-1}) indicating the onset of a sintering process. We have taken into consideration the surface areas when expressing ΔH_{imm} in Figures 2 and 4.

The successive pretreatment of silica at elevated temperatures causes dehydroxylation of the surface. On a partially dehydroxylated surface, the hydroxyl groups undergo hydrogen bonding with their neighboring hydroxyls, and for temperatures above $\sim$400 °C almost all of the hydroxyl groups are of the isolated

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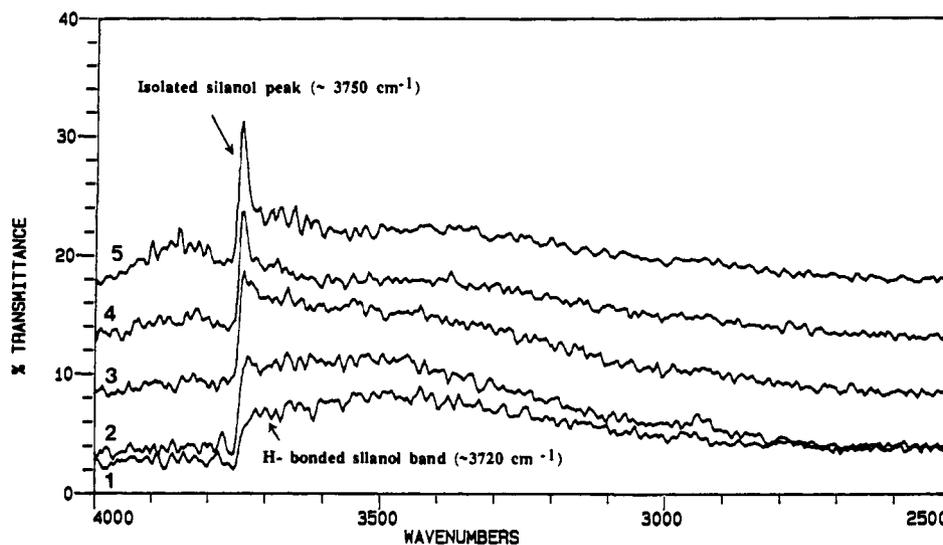(23) Kunath, D.; Schuly, D. *J. Colloid Interface Sci.* **1978**, *66*, 379.

Figure 3. Infrared spectra of silica after pretreatment at elevated temperatures: (a) 150 °C, (2) 300 °C, (3) 400 °C, (4) 500 °C, (5) 600 °C.
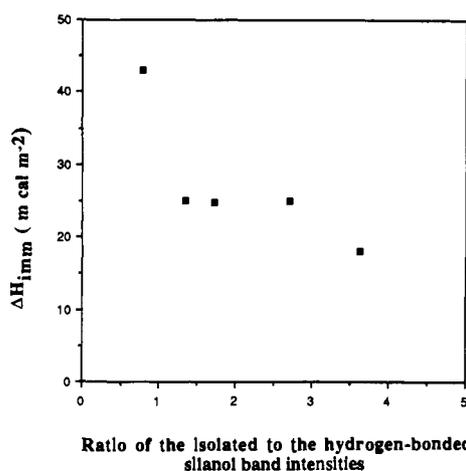

Ratio of the isolated to the hydrogen-bonded
silanol band intensities

Figure 4. Plot of ΔH_{imm} of silica in dichloroacetic acid against the ratios of the isolated to the hydrogen-bonded silanol band intensities at various activation temperatures of silica.

types.[24] Figure 2 presents the variation of the heat of immersion of silica in dichloroacetic acid with the activation temperature. The heat of immersion falls from about 43 mcal m^{-2} to about 25 mcal m^{-2} as the activation temperature is increased from 150 °C to 400 °C. As shown below, this can be related to the interaction of dichloroacetic acid with the hydrogen-bonded silanols. The gradual decrease in the heat of immersion of silica in dichloroacetic acid is due to the corresponding loss of cooperatively hydrogen-bonded silanol groups as the activation temperature is increased. Finally the pretreatment at 1000 °C causes the depletion of the hydroxyls to such a low level that ΔH_{imm} is barely detectable.

Figure 3 shows the FTIR spectra of silica after the solid had been subjected to the series of heat treatments. The sharp peak at ~3750 cm^{-1} is the well-known isolated silanol peak, and the broad band at ~3720 cm^{-1} is due to the hydrogen-bonded silanols.[21] The increase in the intensity of the isolated Si–OH peak in Figure 3, on going from 150 °C to 600 °C is due to the creation of new isolated silanols. Figure 4 shows a plot of the ΔH_{imm} of

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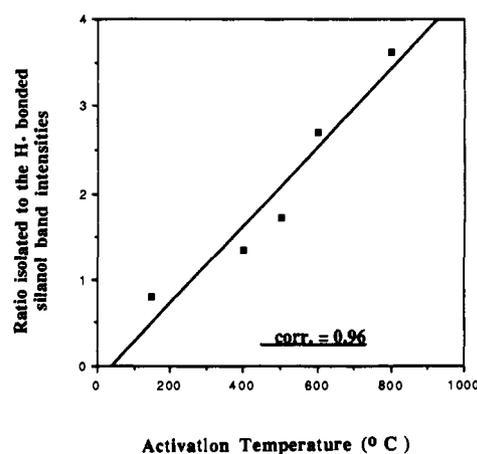

Activation Temperature (° C)

Figure 5. Variation of ratios of isolated to the hydrogen-bonded silanol band intensities with the activation temperature of silica.

silica in dichloroacetic acid against the ratios of the isolated to the hydrogen-bonded silanol band intensities obtained from Figure 3. Finally, Figure 5 shows the close correlation of this ratio to activated temperature and hence to ΔH_{imm} of silica in dichloroacetic acid.

Conclusions

The heats of immersion of a sample of well-characterized silica in a series of acetonitrile solutions of strong Brønsted acids suggest that these strong acids are acting as hydrogen-bond acceptors toward hydroxyl groups on the silica surface. It is proposed that cooperative hydrogen-bonding interactions between silanol groups to each other, or to adsorbed water, produces surface sites that are extremely efficient hydrogen-bond donors. This proposal is supported by an FTIR examination of the surface after activation at a series of increasing temperatures.