Thermochemical Comparisons of Homogeneous and Heterogeneous Acids and Bases. 1. Sulfonic Acid Solutions and Resins as Prototype Brönsted Acids

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Abstract: Heats of ionization by thermometric titration for a series of bases (or acids) can be used to compare solid acids (or bases) with liquid analogues bearing the same functionalities in homogeneous solutions. The method is demonstrated for Brönsted acids by reacting a series of substituted nitrogen bases with solutions of *p*-toluenesulfonic acid (PTSA) in acetonitrile and with suspensions of the microporous polymeric arylsulfonic acid resin–Dowex 50W-X8 in the same solvent. Under well-controlled anhydrous conditions there is a good correlation ($r = 0.992$) between the heats of reaction of the bases with the homogeneous and heterogeneous acid systems, but the homogeneous system gives a more exothermic interaction by 3–4 kcal mol^{-1} for a series of 29 substituted pyridines, anilines, and some other amines. This difference may be attributed to homohydrogen bonding interactions between excess acid and sulfonate anion sites which are more restricted geometrically in the resin than in solution. Other factors which affect the enthalpy change for the acid–base interaction are the acid/base ratio, the water content of the sulfonic acid, the solvent, and the resin structure (e.g., microporous vs. macroporous). Steric hindrance in the base does not differentiate solid from homogeneous acid. In addition to the use of titration calorimetry, heats of immersion are reported for the Dowex–arylsulfonic acid resins and the Nafion–perfluorinated sulfonic acid resin in a series of basic liquids. The results are compared with each other and with those from a previous study of several varieties of coal.

Two of the most common methods for inducing chemical reactions in stable compounds are to heat them or to treat them with acids or bases. However, despite the enormous variety of acidic systems which are in common use, most of our present fundamental knowledge of quantitative acid–base comparisons refers to proton transfer in aqueous solution[1-3] at 25 °C. The past decade has seen considerable expansion of this data base to include several hundred values for proton transfer reactions in the gas phase and in nonaqueous media.[4-11] The following article introduces a strategy for relating homogeneous acid–base systems to heterogeneous ones.

A topic of continual discussion in studies of solid acid–base chemistry is whether the reactive acid sites are functioning primarily as hydrogen bond donors, as proton donors, or as Lewis acids.[12-19] In solution it is now clear that hydrogen bonding,[20-24] proton transfer,[1-4] and Lewis acid complexation[25-29] are different processes and that the response of different classes of bases to them can vary dramatically.[30] Also, it seems reasonable to expect that in solid systems, large changes in basicity orders in relation to those in solution might occur due to different distributions of these types of acid sites, diffusion, and steric factors. In solution, acidic sites of various kinds are in rapid equilibrium with each other and therefore are of nearly the same free energy. However, in a rigid matrix sites of different types and of quite different acidities can be widely distributed with no direct means to be brought into equilibrium through the types of relaxational processes that operate in solution. Obviously, if processes involving solid acid–base interactions are planned on data from an inappropriate homogeneous model system, serious miscalculations may result.

Although a few specialized methods for comparing surface acidities and/or basicities have been advanced[13,17] previously, the most important and commonly used methods are derived from Walling's application of indicator color changes.[31] Using a series of Hammett indicators, he compared a variety of silicas, aluminas, and silica–aluminas by noting which indicators underwent color changes on the surface of these solids. The method has been adopted so generally that most recent reviews[12,16] do not really

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discuss any other approach extensively.

However, the Walling method cannot be used to determine exact H_0 values for solid surfaces because the ionization behavior of a progressive series of indicators on different surfaces cannot be related to a common standard state simply by observing which ones undergo color change. There is no way presently known to generate a continuous related series of increasingly acidic surfaces that is equivalent to the spectrum of aqueous acid solutions used to construct the H_0 scale by overlapping indicator ratios. Furthermore, differences in the physical adsorption of the neutral and acid forms of a series of indicators (such as would correspond to their solution activity coefficients) cannot be compared through the color changes due to their chemisorption on a given acidic surface. Consider, for example, a neutral base B which is more strongly adsorbed on a given surface than is base B′ but whose conjugate acid BH^+ is adsorbed to the same extent as $B'H^+$. Under these circumstances B would exhibit a *lower* basicity than B′ on the surface under study even if their pK_a's in aqueous sulfuric acid solutions were identical.

In addition to this inherent problem, the color change method does not apply well to opaque or colored surfaces, nor to the many bases which are not colored. Furthermore, it does not discriminate well between Lewis and Brönsted acid or hydrogen-bonding sites and makes little allowance for the fact that a given surface may have a variety of sites with different acidities.

Some years ago[32] we initiated a thermochemical approach to circumnavigate many of the problems which had developed in the use of acidity functions for comparing various types of bases. In strongly acidic solutions extrapolation to the aqueous standard state had become dubious for many of the reasons given above for solid systems, but a thermochemical scale of basicity could be generated simply by measuring the heats of reaction of a series of bases with whatever acid system was of interest. In many cases there was a good correlation between the pK_a's of a series of bases when rigorous acidity function methods were used and their heats of ionization in a given strong acid, such as concentrated sulfuric acid or pure FSO_3H.[30] Subsequent work has demonstrated that the same approach may be used for comparing a variety of acids in strongly basic media.[33a,b] The thermochemical method is equally useful for comparing colored and uncolored bases and for Brönsted and Lewis acids.[34a–d]

A thermochemical strategy may now be developed for relating solid acid–base chemistry to that of homogeneous analogues. Heats of reaction of a series of bases with suspension of a given solid acid system would be compared with the heats of reaction of the same bases with homogeneous solutions of an acid bearing the same, or closely analogous, monomeric acid functionality as the solid acid in the same medium.

Our first choice of a system for testing this approach has employed aryl sulfonic acid moieties both in solution and on an ion exchange resin as the heterogeneous analogues.[35] With use of a weakly basic nonhydroxylic solvent, such as acetonitrile, *p*-toluenesulfonic acid may be compared with the sulfonated polystyrene resins.

For the initial comparison of the liquid and solid sulfonic acids, a series of substituted pyridines was chosen which has demonstrated[34] a remarkably uniform pattern of response to ionization by a wide range of Lewis and Brönsted acids in solution and in the gas phase. Since these bases yield excellent linear correlations of free energies and/or enthalpies, they should be a good starting place to test the relationship between free arylsulfonic acid moieties in solution and those constrained by the matrix of a swollen gel structure. If the thermochemical approach were to fail for 3- and 4-substituted pyridines with sulfonic acid resins, there would be little hope for its success with other solid acids. As will be seen below, the method has worked well not only with simple pyridines but also with a wide variety of other nitrogen bases.

Most of the experiments reported here were performed in anhydrous acetonitrile with a large excess of dried sulfonic acid compared to the added base. Control experiments are also reported with widely varied acid-to-base ratios and with different quantities of added water. These factors have significant effects on the results.

Our principal concern has been to test the thermochemical approach for comparing the interactions of a series of organic bases with homogeneous acid solutions and with the most promising solid Brönsted acid system we could think of—a microporous sulfonic acid resin. For further comparison we also report here some more limited studies with a related macroporous sulfonic acid resin, the perfluorinated sulfonic acid resin (Nafion-H), and with a subbituminous coal from an earlier study.[36] Further extension of the method to silica gel (a hydrogen bond donor) and graphite, a nonacidic solid adsorbent, will be reported later.

Experimental Section[64]

(A) General Procedure. The nitrogen bases and the solvents used in this work were available commercially and were purified by standard literature procedures. In general, liquid bases were stirred over potassium hydroxide (KOH) pellets for about 24 h and then fractionally distilled at atmospheric or reduced pressure. Solids were purified by sublimation or recrystallization. The purity of compounds was checked by boiling point or melting point (Thomas Hoover capillary apparatus) and, in some cases, by gas chromatography (Varian 920, 28% Penwalt 223/4% KOH column). A Karl Fischer Automatic Titrimeter System (Fischer Model 392) was used to monitor the water content of compounds, solvents, and reaction mixtures and was calibrated periodically. Anhydrous sulfonic acid samples were stored and weighed out in a nitrogen atmosphere drybox or under a flow of argon. All the titration calorimetry studies reported here were conducted on a Tronac Model 450 calorimeter. Heat of immersion experiments were carried out on a Setaram C-80 heat flow calorimeter.

(B) Sources and Purification of Compounds. (1) Purification and Handling of Solvents. Acetonitrile (MCB, Burdick and Jackson or EM Laboratories) was stirred with anhydrous potassium carbonate for about 24 h and then was fractionally distilled from phosphorus pentoxide (0.05% (w/v)) through an 18 in. Vigreux column under argon. The middle fraction was collected directly in a solvent bottle equipped with an automatic zeroing solvent buret. The freshly distilled solvent was stored under a positive pressure of argon and was used for calorimetry experiments only if its water content was below 80 ppm; bp 81.2–81.5 °C (755 mmHg).

Dimethyl sulfoxide (Aldrich or Burdick and Jackson) was predried over activated 4A Molecular Sieves. It was then treated with 2.4 M *n*-butyllithium in hexane in the presence of a small amount of triphenylmethane indicator until a deep red color appeared. The solvent was fractionally distilled at reduced pressure and then stored under argon. The water content was found to be 76 ppm; bp 29–30 °C (0.05 mmHg).

Chloroform, hexane, methanol, nitromethane, and tetrahydrofuran were purified following standard procedures[37] and were checked by boiling point and stored under argon.

Water was tap water which was deionized with a Continental Water Systems Deionizer.

(2) Drying and Handling of Sulfonic Acid Samples. Analytical grade sulfonic acid ion exchange resin, Bio-Rad AG (Dow) (microporous) 50 W-X8, 20/50 mesh, and macroporous AGMP-50, 200/400 mesh, samples were dried by heating 10–40-g samples at 70–80 °C and a final pressure of <0.05 mmHg for about 48 h.[38] After being dried, the 20/50 mesh sample was used as such whereas the 200/400 mesh sample was screened to 200/325 mesh. The exchange capacities of the dried samples were determined by titrating them against a standard 0.1 N NaOH solution. The exchange capacities were found to be 5.13 ± 0.06 and 4.42 ± 0.05 mequiv/g for 20/50 mesh and 200/325 mesh samples, respectively.

p-Toluenesulfonic acid (Fisher, monohydrate sample) was dehydrated by heating at 50 °C and a final pressure of <0.05 mmHg for about 120

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h.[39] The sulfonic acid samples were stored and handled in a nitrogen atmosphere drybox.

(3) Conversion of Nafion K^+ Form to Nafion H^+ Form. The K^+ form resin (8 g) (511X-DuPont experimental perfluorinated ion-exchange resin with particle size distribution: 12 mesh to 140 mesh) was placed in 20 mL of 4 N HCl, and the mixture was stirred at room temperature for 4 to 6 h.[40,41] The resin was then filtered and washed with deionized water. Four such treatments were given. After the final exchange, the resin was washed thoroughly with water until the filtrate was neutral and gave a negative test for chloride ion. The resulting solid was dried in a vacuum oven at 70–80 °C for about 24 h. The dried sample of Nafion-H was sieved to 45/60 mesh in a drybox. The exchange capacity of Nafion-H was determined by titrating it against a standard NaOH solution. The exchange capacity of Nafion-H was found to be 0.89 ± 0.01 mequiv/g which is slightly greater than that (0.8 mequiv/g) obtained by Delmas et al.[42]

(C) Calorimetry. Heats of reaction of *p*-toluenesulfonic acid and the polymeric sulfonic acid samples with various bases were measured in nonaqueous media by thermometric titration. The operation of the calorimeter was checked periodically by measuring the heat of protonation of an aqueous solution of THAM [tris(hydroxymethylaminomethane)] with a standard aqueous hydrochloric acid solution.[43]

In each calorimetric run the basic solution of known concentration (0.2–0.3 M) from the calorimeter buret was reacted with approximately 10–15-fold excess (5 mequiv) of *p*-toluenesulfonic acid or acid resin and 35 mL of solvent which was in the calorimeter reaction vessel. The operation of the Tronac 450 titration calorimeter has been described previously.[34b,43,44] All experiments with this calorimeter were conducted in the isoperibolic mode at 25.0 °C. Each reported ΔH_{rxn} is the average of at least five and usually seven or more enthalpy measurements. The reproducibility of the experimental results was verified by using different samples of resin, base, and acetonitrile. When performing measurements on suspensions of polymeric resin, the design and placement of the stirrer were found to be critical in achieving uniform mixing. A clear glass Dewar was used to observe the mixing abilities of various stirrers. Aliquots of the reaction mixture were analyzed for water content by Karl Fischer titration. The contents of the reaction vessel were maintained under a blanket of argon throughout a calorimetric experiment.

Heats of immersion were measured on a Setaram C-80 heat flow calorimetry (Astra Scientific International, Santa Clara, CA) which is built to operate up to 300 °C on the Tian-Calvet heat flow principle. It was operated as described previously.[36]

The performance of the two calorimeters (Tronac 450 and Setaram C-80) was checked by measuring the heat of reaction of pyridine with Dowex 50W-8X in acetonitrile at 25 °C. Excellent agreement between the two is shown below:

$$\Delta H(\text{Setaram}) = -14.44 \pm 0.12\ \text{kcal/mol}$$

$$\Delta H(\text{Tronac}) = -14.60 \pm 0.27\ \text{kcal/mol}$$

Titration experiments examining the effect of added water on the heats of ionization of pyridine by the polymeric acid resin and PTSA were conducted as described above except that known amounts of water were added to the calorimeter reaction vessel prior to making the enthalpy measurements. Most of the experiments conducted in THF were carried out on a batch calorimeter which has been described elsewhere.[34d]

In acid/base ratio studies experiments were designed to cover a wide range of acid/base ratios from a large excess of acid to nearly a 1:1 ratio. This involved using several stock solutions of acid in which the initial concentration of acid was varied.

Results

(A) Microporous vs. Macroporous. Microporous resins are prepared by a suspension polymerization procedure which involves agitating styrene and divinylbenzene monomers in an aqueous medium. The particle size of individual resin beads depends on the polymerization conditions and may be varied to produce beads with diameters ranging from 1 mm to less than 0.04 mm or in terms of mesh size from 16 mesh to greater than 400 mesh. On a microscopic scale the resulting copolymer is a homogeneous structure with no discontinuities when dry.[45] When the resin is sulfonated, the acidic sites are distributed statistically throughout the interior of each resin particle. The accessibility of the sulfonic acid groups in a microporous resin depends on a number of factors including the capability of the resin to swell in the environment in which it is placed. If the resin beads are completely dry, the polymer matrix is collapsed and it is impervious to any liquid unable to serve as a swelling medium. In general, microporous[45-50] or gel-type resins in a swollen state have surface areas of less than 0.1 m^2/g of exchanger.[50]

Macroporous or macroreticular ion-exchange resins possess rigid polymer matrices which do not collapse upon drying. Macroporous resins are prepared in an organic medium by a polymerization process which leaves pores several hundred angstroms in diameter. As a result, macroporous resins are heterogeneous structures whose beads are composed of two distinct phases—a gel phase consisting of agglomerates of randomly packed microspheres which collapse upon drying and macropores which are part of the rigid polymer matrix and exist whether or not the gel phase is in a swollen state. Macroreticular resins have a high internal surface area, greater than 50 m^2/g, and the acid sites in sulfonated copolymers are accessible even without swelling.[45,47,50,51]

The structure of the polymeric matrix affects the kinetics of proton transfer. Rate-controlling diffusion is the combination of two terms: diffusion through a layer of solvent adhering to the resin bead (Nernst diffusion) and diffusion into the resin bead (particle diffusion). Particle diffusion is the major factor determining the rate, and it is influenced by such properties of the resin as the particle diameter, the degree of cross-linking, and the ability of the solvent to swell the resin. This final factor is particularly important for microporous resins.[46,47,52]

For microporous resins the presence or absence of water may determine whether the polymeric matrix is swollen or collapsed. In addition, the chemical nature of the sulfonic acid group changes from that of an anhydrous acid to that of a solvated proton as water is added to the system.

Numerous methods, involving different combinations of temperatures and pressures, have been employed to dry various resins.[53-60] The drying conditions employed for resin samples used in the work were those used by Gordon and Pietrzyk for resins of similar structure.[55-59]

(B) Heats of Reaction in Anhydrous Acetonitrile. (1) Variations of Acid–Base Ratio. In contrast to a simple acid/base reaction in aqueous solution, thermometric titrations of sulfonic acids in nonaqueous media displayed a trend of decreasing heats of reaction as the ratio of acid to base varied from infinity to 1/1. In these cases, the measured differential enthalpy values ($\Delta H_{\mathrm{exptl}}$) going from one acid base (A/B) ratio to another differs from the *calculated integral enthalpy* of reaction ($\Delta H_{\mathrm{calcd}}$) which would be obtained by going from an initial A/B ratio of infinity to the first

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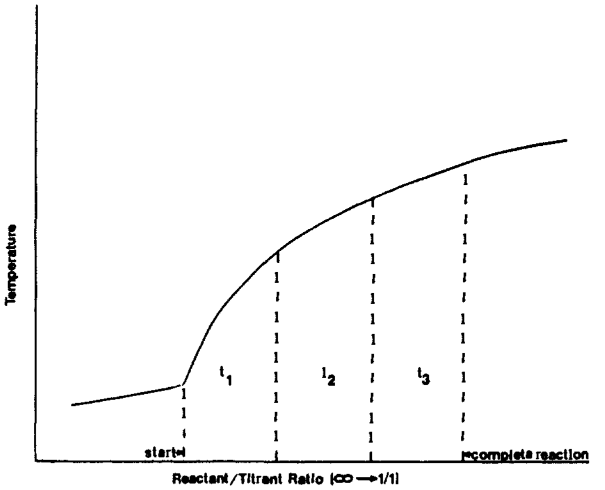


Figure 1. Diagram of temperature vs. reactant/titrant ratio for comparing the continuous and incremental addition methods used in titration calorimetry.

Table I. Heats of Reaction (kcal mol^{-1}) of PTSA with Pyridine as a Function of Acid/Base Ratio in Acetonitrile at 25 °C

range of A/B ratio	differential $-\Delta H_{\text{exptl}}$	from ∞ to fixed A/B ratio	integral $-\Delta H_{\text{calcd}}$
∞ → 44.0/1	18.26	44/1	18.26
44.0/1 → 22.6/1	18.48	22.6/1	18.37
15.3/1 → 11.6/1	18.30	11.6/1	18.35
9.3/1 → 7.8/1	17.78	7.8/1	18.18
6.6/1 → 4.4/1	17.16	4.4/1	17.63
3.3/1 → 2.7/1	16.08	2.7/1	17.13
2.2/1 → 1.9/1	15.00	1.9/1	16.61
1.5/1 → 1.2/1	13.97	1.2/1	15.81
1.2/1 → 1.1/1	13.29	1.1/1	15.45

A/B ratio shown by scanning the differential steps.

The addition of an increment of titrant corresponds to determining a heat of reaction along a portion of a continuous titration curve. An example is shown in Figure 1 where the reactant/titrant ratio as a function of added base may be determined from the initial concentration of the reactant and the number of moles of titrant added. The average enthalpy of reaction across a concentration range from infinity to a *fixed reactant/titrant ratio* may be calculated from the experimentally *measured differential values*.

All of the thermometric measurements used to compare the strengths of different bases with different types of sulfonic acids were performed in the presence of a large excess of acid to base. In addition, several studies were conducted where the concentration range was extended over the entire acid/base ratio from infinity to as near to unity as possible. The data in Table I present the enthalpies of reaction of PTSA, with pyridine in anhydrous acetonitrile as a function of the acid/base ratio. Tables II and III contain corresponding enthalpy data in acetonitrile for the reactions of Dowex 50W-X8, 20–50 mesh, and Dowex MP-50, 200–325 mesh, with pyridine.

The data given in Table I for the reaction of pyridine with PTSA in acetonitrile indicate that the enthalpy of the interaction is less exothermic at an acid/base ratio approaching 1/1 than in the presence of a large excess of acid and that the magnitude of the decrease in the enthalpy value is about 3 kcal/mol. In contrast, the experimental results listed in Table II for the reaction of microporous Dowex 50W-X8, 20–50 mesh, with pyridine in acetonitrile do not indicate a concentration dependence for the enthalpy of this interaction. However, there was no detectable reaction between the resin and pyridine below an acid/base ratio of about 3/1.

The heats of reaction of pyridine with macroporous Dowex MP-50, 200–325 mesh, in acetonitrile which are given in Table III show a concentration dependence at acid/base ratios below about 10/1 for the interaction of the resin and the base. The magnitude of the enthalpy decrease is about 3 kcal/mol across the concentration range studied. Similar small decreases were seen for titrations in several other solvents.

Table II. Heats of Reaction of Dowex 50W-X8 with Pyridine as a Function of Acid/Base Ratio in Acetonitrile at 25 °C[a]

range of A/B ratio	$-\Delta H_{\text{exptl}}$ (kcal/mol)
∞ → 100.4/1	15.77
∞ → 51.3/1	15.59
∞ → 50.4/1	15.77
100.4/1 → 36.0/1	15.85
50.4/1 → 22.9/1	15.63
23.4/1 → 15.8/1	15.28
22.9/1 → 14.8/1	15.58
8.3/1 → 5.5/1	14.85
5.5/1 → 4.2/1	slow
4.2/1 → 3.6/1	slow
<3/1	0

[a] These runs employed a different sample of resin than was used for the measurements in Table IV.

Table III. Heats of Reaction of Dowex MP-50 with Pyridine as a Function of Acid/Base Ratio in Acetonitrile at 25 °C

range of A/B ratio	$-\Delta H_{\text{exptl}}$ (kcal/mol)
∞ → 82.9/1	18.49
∞ → 55.3/1	18.46
∞ → 53.7/1	18.88
82.9/1 → 41.8/1	18.53
55.3/1 → 27.8/1	18.65
27.9/1 → 21.1/1	18.37
17.2/1 → 8.6/1	16.81
5.8/1 → 4.3/1	16.93
4.8/1 → 2.4/1	15.80
2.4/1 → 1.6/1	12.12
1.6/1 → 1.2/1	slow

Although there are large differences in the heats of reaction between these vastly different media, all show decreases of 2–4 kcal/mol between ΔH_{rxn} at the highest acid/base ratio and the lowest even when the ultimate 1/1 ratio could not be reached.

(2) Microporous Dowex 50W-X8, 20–50 Mesh. The heats of reaction, ΔH_{rxn}, for 29 bases including substituted pyridines, anilines, and aliphatic amines with dry microporous Dowex 50W-X8, 20–50 mesh, have been measured in anhydrous acetonitrile at 25 °C and appear in Table IV. For comparison, the enthalpy values obtained for the reaction of PTSA with the same bases under analogous conditions are also listed. These titration calorimetry runs were conducted on the Tronac 450 as described in the Experimental Section in the presence of a greater than 10-fold excess of acid. Under these conditions, there is no decreasing trend in the data as a function of the acid/base ratio, but because rates of diffusion into the resin differ, the shapes of the thermograms for the heterogeneous systems usually differed from those for the usual titration of liquid base into acid solutions as were observed for PTSA. As shown in the final column of Table IV, the enthalpies of reaction of the various bases with PTSA are generally 3 to 4 kcal/mol more exothermic than the same reactions with the microporous resin.

(3) Macroporous Dowex MP-50, 200–325 Mesh. The reproducibility of the titration calorimetry results for a macroporous sulfonic acid resin, Dowex MP-50, 200–325 mesh, was also investigated with use of the heat of reaction of various samples of the dry resin with pyridine in anhydrous acetonitrile. A slight decreasing trend in the measured heats of reaction was observed even at acid/base ratios of greater than 15/1, and the enthalpy values are quite sensitive to even small quantities of water.

The heats of reaction of six bases with macroporous Dowex MP-50, 200–325 mesh, measured in acetonitrile at 25 °C are listed in Table V. The ΔH_{rxn}'s presented are the average of the measured incremental values across acid/base ratios from infinity to about 15/1.

(C) Solvent Effect Studies. The influence of the reaction medium on the thermochemical behavior of the microporous and

Table IV. Aqueous pK_{BH^+} and Heats of Reaction (kcal mol^{-1}) of Various Bases with PTSA and Dowex 50W-X8, 20–50 Mesh, in Acetonitrile at 25 °C

	bases	pK_{BH^+}	$-\Delta H_{Dowex}$	$-\Delta H_{PTSA}$	$\Delta\Delta H_{rxn}$
1.	3,5-dichloropyridine	0.67[b]	7.47 ± 0.41	11.08 ± 0.28	3.61
2.	4-cyanopyridine	1.9[a]	10.04 ± 0.23	14.34 ± 0.12	4.30
3.	3-bromopyridine	2.9[a]	11.60 ± 0.05	15.25 ± 0.08	3.65
4.	4-carbomethoxypyridine	3.5[b]	11.71 ± 0.06	16.11 ± 0.19	4.40
5.	pyridine	5.2[a]	14.60 ± 0.27	18.62 ± 0.36	4.02
6.	2-methylpyridine	5.17[a]	16.75 ± 0.37	19.21 ± 0.66	2.46
7.	3-methylpyridine	5.68[a]	14.82 ± 0.79	19.19 ± 0.92	4.37
8.	4-methylpyridine	6.0[a]	15.35 ± 0.18	19.58 ± 0.20	4.23
9.	2,6-dimethylpyridine	6.7[a]	16.11 ± 0.11	20.32 ± 0.13	4.21
10.	2,4-dimethylpyridine	6.8[a]	16.15 ± 0.13	20.05 ± 0.10	3.90
11.	2,4,6-trimethylpyridine	7.4[a]	17.18 ± 0.37	21.17 ± 0.72	3.99
12.	2,6-diethylpyridine	6.7[b]	17.93 ± 0.23	20.17 ± 0.10	2.24
13.	2,6-di-*tert*-butylpyridine	4.95[d]	13.87 ± 0.58	16.44 ± 0.35	2.57
14.	3-nitroaniline	2.5[a]	10.23 ± 0.18	14.16 ± 0.37	3.93
15	2,6-dimethylaniline	3.9[a]	12.58 ± 0.40	16.11 ± 0.11	3.53
16.	2,4,6-trimethylaniline	4.4[a]	14.02 ± 0.10	11.27 ± 0.15	3.25
17.	aniline	4.6[a]	13.30 ± 0.13	17.17 ± 0.14	3.87
18.	3,4-dimethylaniline	5.2[a]	15.08 ± 0.15	18.3 ± 0.15	3.27
19.	*N*,*N*-dimethyl-3-nitroaniline	2.6[a]	9.70 ± 0.18	13.46 ± 0.16	3.76
20.	*N*,*N*-dimethylaniline	5.1[a]	14.01 ± 0.18	17.19 ± 0.25	3.18
21.	*N*,*N*-diethylaniline	6.6[a]	15.22 ± 0.37	18.75 ± 0.18	3.53
22.	triethylamine	10.7[a]	22.85 ± 0.19	27.06 ± 0.16	4.21
23.	*tert*-octylamine	10.6[c]	25.59 ± 0.31	28.80 ± 0.36	3.21
24.	*n*-octylamine	10.6[c]	26.41 ± 0.10	28.51 ± 0.54	2.10
25.	1-(*N*,*N*-dimethylamino)naphthalene	4.83[a]	15.37 ± 0.31	17.01 ± 0.40	1.64
26.	i-propylamine	10.63[e]	29.43 ± 0.62	32.52 ± 0.91	3.09
27.	pyrrolidine	11.27[a]	23.04 ± 1.06	26.57 ± 0.53	3.53
28	quinuclidine	10.95[a]	26.58 ± 0.61	29.12 ± 2.25	2.54
29.	*tert*-butylamine	10.45[e]	27.04 ± 0.30	28.68 ± 0.46	1.64

[a] Reference 3. [b] Fischer, A.; Galloway, W. J.; Vaughan, J. *J. Chem. Soc.* **1964**, 3591. [c] Perrin, D. D.; Dempsey, B.; Sergeant, E. P. *pK$_a$ Predictions for Organic Acids and Bases*; Chapman and Hall: New York, 1981. [d] Hopkin, H. P., Jr.; Jahagirdar, D. V.; Moulik, P. S.; Aue, D. H.; Webb, H. M.; Davidson, W. Rr.; Pedley, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 4341. [e] Hall, H. K., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 5441.

Table V. Heats of Reaction of Various Bases with Dowex MP-50 in Acetonitrile at 25 °C and Heats of Immersion of Dowex MP-50 at 25 °C and Nafion into the Same Bases

			$-\Delta H_{imm}$ (kcal equiv^{-1} of acid)	
base	pK_{BH^+}	$-\Delta H_{rxn}$ (kcal mol^{-1} of base)	Dowex MP-50	Nafion[c]
ethylenediamine	9.9/6.8[a]	50.30 ± 1.20	33.01 ± 0.32	37.17 ± 0.72
n-octylamine	10.6[b]	28.88 ± 0.26	29.63 ± 0.21	36.70 ± 0.69
n-hexylamine	10.6[b]	27.90 ± 0.25	29.40 ± 0.30	
2,6-dimethylpyridine	6.7[a]	19.30 ± 0.16		
4-methylpyridine	6.0[a]		18.23 ± 0.16	20.72 ± 0.28
pyridine	5.2[a]	18.22 ± 0.46	17.18 ± 0.30	19.42 ± 0.28
aniline	4.6[a]	16.40 ± 0.39	16.88 ± 0.17	
dimethylsulfoxide			11.11 ± 0.04[d]	13.45 ± 0.28
acetonitrile			3.89 ± 0.04	4.28 ± 0.28
hexane			0.34 ± 0.04[d]	0.60 ± 0.02
aqueous tetrabutylammonium hydroxide (1.47 M)			29.43 ± 0.33[d]	27.01 ± 0.45[d,e]
aqueous sodium hydroxide (1 M)			23.07 ± 0.28	16.72 ± 0.22
water			10.27 ± 0.22	4.58 ± 0.28

[a] Reference 3. [b] Perrin, D. D.; Dempsey, B.; Sergeant, E. P. pK_a Predictions *for Organic Acids and Bases*; Chapman and Hall: New York, 1981. [c] ΔH_{imm} values for Nafion are at 30 °C. [d] ΔH_{imm} values at 80 °C. [e] Reaction between Nafion and highly viscous aqueous tetrabutylammonium hydroxide was extremely slow at 30 °C.

macroporous resins was examined by measuring the heats of reaction of pyridine with samples of the resins in eight solvents. The enthalpy measurements were carried out in the solvents listed in Table VI in the presence of a greater than 10-fold excess of acid with dry microporous resin, Dowex 50W-X8, 20–50 mesh, and dry macroporous resin, Dowex MP-50, 200–325 mesh.

For the microporous resin, it was possible to measure enthalpy values only in acetonitrile, methanol, and water, since only these solvents were able to swell the resin. In tetrahydrofuran (THF), the first one or two injections of base (about 0.1-mequiv increments) into the Dewar flask containing a suspension of about 5 mequiv of resin in 35 mL of THF produced a small, slow heat evolution. Subsequent additions, performed immediately or after several hours had elapsed, showed no further heat evolution. This behavior was reproducible from one titration calorimetry run to another. The remaining solvents listed in Table VI displayed no detectable heat of reaction for the interaction of pyridine and Dowex 50W-X8 under the conditions described above.

Table VI. Heats of Reaction of Microporous and Macroporous Resin Samples with Pyridine in Various Solvents at 25 °C

	$-\Delta H_{rxn}$ (kcal/mol)	
solvent	Dowex 50W-X8	Dowex MP-50
dimethyl sulfoxide	not detectable	8.16 ± 0.24
water	7.79 ± 0.30	8.83 ± 0.40
methanol	8.51 ± 0.09	9.36 ± 0.28
tetrahydrofuran	not measurable	17.77 ± 0.35
acetonitrile	15.57 ± 0.16	18.22 ± 0.46
nitromethane	not detectable	21.08 ± 1.24
chloroform	not detectable	22.39 ± 1.61
hexane	not detectable	23.21 ± 2.22

The ΔH_{rxn}'s of pyridine with the macroporous resin were measured in eight solvents and often showed a dependence on the ratio of acid to base even in the presence of a large excess of acid (i.e., when the acid/base ratio was varied from infinity to about

Table VII. The Effect of Added Water on the Heats of Ionization of Pyridine with Dowex 50W-X8 and PTSA in Acetonitrile at 25 °C

acid	$-\Delta H_i$ (kcal/mol)	mole ratio (H_2O/acid)
Dowex 50	14.60 ± 0.34	
Dowex 50	12.70 ± 0.21	0.5
Dowex 50	10.15 ± 0.11	1.0
Dowex 50	9.47 ± 0.26	2.1
Dowex 50	7.53 ± 0.18	5.2
Dowex 50	5.92 ± 0.10	11.4
PTSA	18.68 ± 0.36	
PTSA	16.40 ± 0.70	0.5
PTSA	15.03 ± 0.64	1.0
PTSA	11.00 ± 0.37	2.2
PTSA	6.04 ± 0.33	5.6
PTSA	5.04 ± 0.15	10.3

10/1). The averages of the measured incremental enthalpy values are reported in Table VI.

(D) Water Addition Studies. The results of a titration calorimetry study examining the effect of added water on the heats of ionization of pyridine by microporous Dowex 50W-X8 and PTSA in acetonitrile are presented in Table VII.

(E) Heats of Reaction by Batch Calorimetry in Wet THF. Table VIII presents a batch calorimetry investigation employing the monohydrate form of PTSA and wet Dowex 50W-X8, 20–50 mesh, which was stored in a humidistat. Again, the heat of reaction in THF is consistently 4 to 6 kcal/mol more exothermic for the interaction of PTSA with a series of substituted pyridines in the presence of a larger excess of acid than for the same interactions in the heterogenous system.

The moisture content of the two sulfonic acid systems was controlled so that the heterogeneous system contained about 5% (v/v) water in THF while the homogeneous system contained about 0.5% (v/v) water in THF.

(F) Heats of Immersion. The final columns in Table V present heats of immersion, ΔH_{imm}, of the dry macroporous resin and Nafion into the same bases used in the titration calorimetry investigation. In contrast to the heats of reaction from titration calorimetry, the heats of immersion were obtained under conditions of excess base in the Setaram C-80 heat flow calorimeter and are reported in kcal/equiv of acid sites on the resin.

Discussion

The principal goal of this study has been to test the possibility of using heats of reaction of a series of bases with an appropriate homogeneous acidic solution as a quantitative model for the acidic behavior of a solid bearing the same acidic functionalities as those in solution. In the course of our attempts to find standard conditions for using *p*-toluenesulfonic acid (PTSA) as a model for sulfonic acid resins, we learned that the heats of reaction were affected by the solvent, the presence of water (even to very low concentrations), the structure of the resin, and the relative proportions of acid and base which were brought into reaction. In the following discussion of our results we shall first present the evidence that, when conditions are controlled properly, acetonitrile solutions of PTSA are an excellent model for the acidic properties of preswollen microporous sulfuric acid resin slurries. We shall then consider evidence that homohydrogen bonding interactions between the sulfonate anion and excess acidic sites are responsible for a constant difference between heats of reaction for bases with the homogeneous and the heterogeneous acids. The role of the other variables listed above will be considered and, finally, comparison between the results of this work and those from other relevant thermochemical acid–base studies will be made.

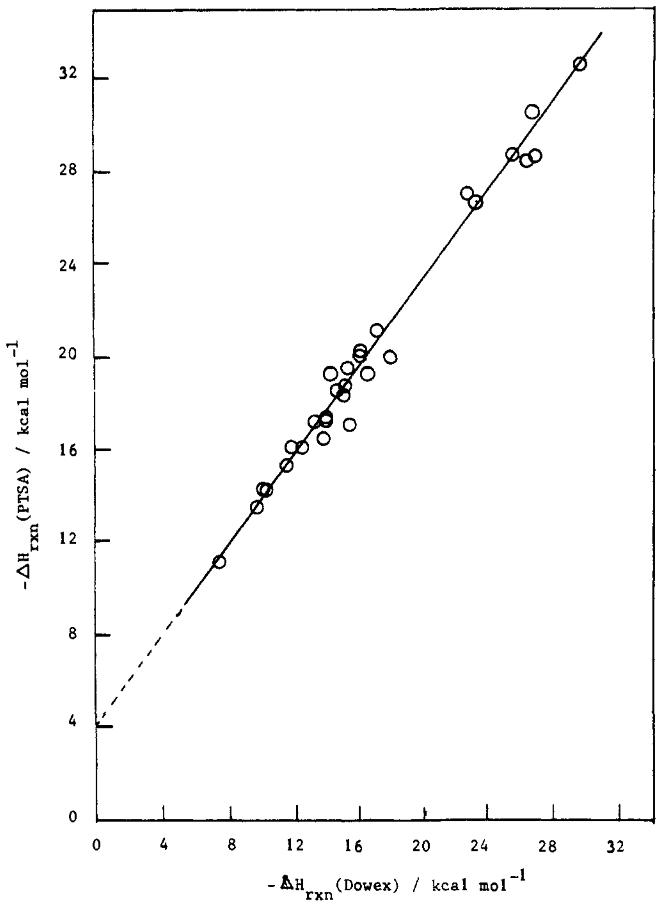


Figure 2. Correlation for heats of reaction of 29 nitrogen bases in Table IV with excess *p*-toluenesulfonic acid and microporous sulfonic acid resin Dowex 50W-X8 in acetonitrile at 25 °C.

Comparison of PTSA with Microporous Dowex 50W-X8–Sulfonic Acid Resin. Figure 2 exhibits the strongest evidence for the general soundness of the thermochemical approach for comparing the acidity of this heterogeneous resin system with its homogeneous model. The most obvious characteristics of this plot are the following: (a) its overall linearity covering a range of nearly 20 kcal/mol for amine bases of widely varied structures; (b) its nearly unit slope; and (c) its intercept at 4.46 kcal/mol on the $-\Delta H_{\text{rxn}}$(Dowex) axis which represents a regular difference of 3–4 kcal/mol between the heat of reaction of each base with solutions of PTSA and the corresponding slurries of the resin acid. Even though there are wide structural differences, the largest departures from the overall correlation line are only 2 kcal/mol.

Linear regression analysis of the complete data set for all 29 base yields the equation

Table VIII. Aqueous pK_{BH^+}'s and Heats of Reactions of Substituted Pyridines by Batch Calorimetry with PTSA and Dowex 50W-X8 in Wet THF at 25 °C

base	pK_{BH^+}[a]	$-\Delta H_{\text{rxn}}$(Dowex) (kcal/mol)	$-\Delta H_{\text{rxn}}$(PTSA) (kcal/mol)	$\Delta\Delta H$
3-chloropyridine	2.8	2.84 ± 0.14	8.37 ± 0.5	5.53
3-bromopyridine	2.9	2.61 ± 0.27	7.57 ± 0.23	4.96
4-carbomethoxypyridine	3.5	4.21 ± 0.08	9.19 ± 0.15	4.98
pyridine	5.2	7.76 ± 0.07	13.10 ± 0.09	5.34
2-*tert*-butylpyridine	5.8	7.01 ± 0.15	12.59 ± 0.10	5.58
4-*tert*-butylpyridine	6.0	7.48 ± 0.40	11.37 ± 0.10	3.89
2-methylpyridine	6.0	8.58 ± 0.40	14.45 ± 0.21	5.87
2,6-dimethylpyridine	6.7	9.08 ± 0.23	13.45 ± 0.32	4.37
2,4,6-trimethylpyridine	7.4	10.63 ± 0.14	15.11 ± 0.23	4.48

[a] Reference 3.

$$\Delta H_{\mathrm{rxn}}(\mathrm{PTSA}) = -4.46 \pm 0.935\Delta H_{\mathrm{rxn}}(\mathrm{Dowex}) \qquad (1)$$

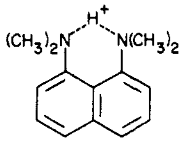
while the corresponding equation for the subset of pyridines, including those substituted at the 2- and 6-positions, gives the equation

$$\Delta H_{\mathrm{rxn}}(\mathrm{PTSA}) = -4.72 + 0.927\Delta H_{\mathrm{rxn}}(\mathrm{Dowex}) \qquad (2)$$

The correlation coefficients for the two equations are respectively 0.992 and 0.964.

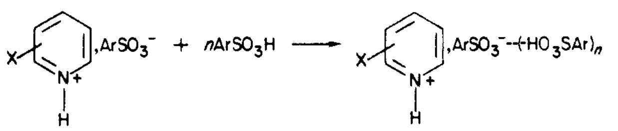
Differential steric factors are of obvious interest in comparing the more restricted geometry of the resin with the homogeneous system. However, steric discrimination even for the classical comparisons[61] of 2,6-di-*tert*-butyl pyridine vs. 2,6-lutidine or of triethylamine vs. quinuclidine is only marginal. Thus, in the first case, ΔH_{rxn}(Dowex)'s calculated by eq 1 and 2 are −12.97 and −12.85 kcal/mol compared to the actual value of −13.87 ± 0.58 kcal/mol. In contrast the calculated value for quinuclidine, based on the total set of bases, is −24.86 kcal/mol compared to the more exothermic measured value of −26.58 kcal/mol. Its sterically hindered cognate triethylamine gives a measured ΔH_{rxn}(Dowex) of −22.85 ± 0.19 kcal/mol which is only slightly less exothermic than the −21.38 kcal/mol calculated by eq 1.

A different type of steric factor is represented by "proton sponge", 1,8-bis(dimethylamino)naphthalene, whose unusually high basicity[62] is attributable to the special stability of the internally solvated proton trapped between the adjacent dimethylamino groups. If dimethylaniline (ΔH_{rxn}(PTSA) = −16.92 ± 0.40 kcal/mol) or naphthylamine (−15.37 ± 0.31 kcal/mol) are models for monoprotonating "proton sponge", its value of −26.02 ± 0.34 kcal/mol is spectacularly high. However, if its isomer 1,5-bis(dimethylamino)naphthalene is chosen as the model (ΔH_{rxn}(PTSA) = −32.60 ± 0.90 kcal/mol), "proton sponge" is surprisingly weak.



The choice between these assignments can be made by noting that the difference (ΔH_{rxn}(PTSA) − ΔH_{rxn}(Dowex)) for the 1,8-isomer is −3.59 kcal/mol which is in the normal range for monoprotonated amines while the corresponding value for the 1,5-isomer is −6.04 kcal/mol, almost twice the normal monoprotonation value. If one chooses, *N,N*-dimethylaniline as a model for monoprotonation, one obtains (by doubling its values) estimates of ΔH(PTSA) = −33.84 kcal/mol, ΔH(Dowex) = −27.78 kcal/mol, and $\Delta\Delta H$ = −6.06 kcal/mol which are close to the observed values for protonation of the 1,5-isomer of proton sponge. Thus, the strength of the hydrogen bond from monoprotonation of the 1,8-isomer appears to be too strong to sacrifice by diprotonation.

Homohydrogen Bonding of the Sulfonate Anion. A striking feature of Figure 2, Table IV, and eq 1 and 2 is the reproducible difference of −3 to −4 kcal/mol for ΔH(PTSA) − ΔH(Dowex) for all of the monobasic amines. Clearly this difference has little to do with the structure of the base and, as we shall see below, it is affected but little by any factor except the acid/base ratio. These facts and a wealth of published studies on acid–base behavior in nonhydroxylic solvents[4,21,63] are interpreted readily in terms of a strong hydrogen bonding stabilization of the sulfonate anion by excess sulfonic acid sites. The stability of hydrogen-bonded complexes in acetonitrile is about 3 kcal/mol for methanesulfonic acid and 2,5-dichlorobenzenesulfonic acid.[63]



This type of interaction is not so important for proton-transfer reactions in aqueous media due to strong solvation of the anion by water. In acetonitrile, the anion derives insufficient stabilization from solvation and, in the presence of excess acid, resorts instead to hydrogen-bonding interactions with the parent acid. In homogeneous solution, a sulfonate anion has little restriction to stabilization by excess sulfonic acid, but this should be more difficult for sulfonate anions and their conjugate acids anchored to a polymeric backbone. The extent of homoconjugation available to the sulfonic acid groups of a resin suspended in acetonitrile should be related to the structure of the resin and to such factors as the degree of sulfonation, the degree of cross-linking, the degree of swelling of the resin by the solvent, and the surface area.[59]

Support for this interpretation is found in Tables I and II which show that as the acid/base ratio approaches unity the difference between the homogeneous and heterogeneous systems not only decreases but converges on a common value. At a ratio of 1/1, in the absence of excess acid for homoconjugative stabilization, the reaction between pyridine and PTSA in acetonitrile yields a reaction enthalpy of about 15 kcal/mol which is close to ΔH_{rxn} of pyridine with the suspended microporous resin. Also, reverse addition experiments were conducted such that PTSA was titrated into solutions of excess pyridine in acetonitrile, and again the resulting enthalpy value also was about 15 kcal/mol.

Variation of acid/base ratio for pyridine with macroporous resin MP-50 in a variety of solvents and with microporous 50W-X8 with water shows similar patterns of declining exothermicity as the excess acid concentration available for homohydrogen bonding is reduced.

If homohydrogen bonding is used as the single factor for interpreting differences between the behavior of different acids, one is led to an interesting conclusion about macroporous MP-50 from the data in Table V. Taking pyridine as a case in point, one notes that its ΔH_{rxn} for titration of an acetonitrile solution of this base into excess MP-50 yields −18.22 kcal/mol; corresponding closely to −18.62 kcal/mol for its ΔH_{rxn} with excess PTSA in Table IV. This suggests that for some reason homohydrogen bonding interactions between sulfonic acid residues are feasible for the macroporous resin but not for the microporous resin. Supporting evidence is supplied from the heats of immersion experiments (Table V) where samples of dried macroporous MP-50 are released into an excess of each base. If one corrects the value for pyridine (ΔH_{rxn} = −17.18 kcal/equiv) by the value for acetonitrile (−3.89 kcal/mol) to compare it with heats of reaction in this solvent, one obtains −13.29 kcal/equiv which is reasonably close to $\Delta H_{\mathrm{Dowex}}$ = −14.60 kcal/mol for pyridine with excess *microporous* resin which we have argued is unable to give homohydrogen bonding. Thus, the macroporous resin behaves with base like PTSA when it is in excess but like microporous resin when there is excess base. We know of no independent evidence to test this hypothesis.

Solvent Effects. Solvent effects on the heats of protonation of pyridine with microporous Dowex 50W-X8, 20–50 mesh, and macroporous Dowex MP-50, 200–325 mesh, show that the effective acidities of both resins are strongly dependent on their environment. This supports the previous results of Wilks and Pietrzyk.[59]

The results for the dry microporous resin are reported in Table VI and show that in most anhydrous organic solvents studied, the dry polymer matrix apparently does not swell sufficiently to render its acidic sites accessible. Even after several hours, no heat of reaction was detected between pyridine and samples of the resin in hexane, chloroform, dimethyl sulfoxide, and nitromethane. A small, slow heat evolution was observed in tetrahydrofuran, but it was not measurable. Only in water, methanol, and acetonitrile did swelling of the polymer permit a measurable acid–base reaction

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[61] 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.

[62] Alder, R. W.; Bowman, P. S.; Steele, W. R. S.; Winterman, D. R. *J. Chem. Soc., Chem. Commun.* **1968**, 723.

[63] Coetzee, J. F. In *Progress in Physical Organic Chemistry*; Streitwieser, A., Jr., Taft, R. W., Eds.; John Wiley and Sons: New York, 1967; Vol. 4, pp 45–93.

[64] For further details see the Doctoral Thesis of R. A. Haaksma, Duke University, 1985.

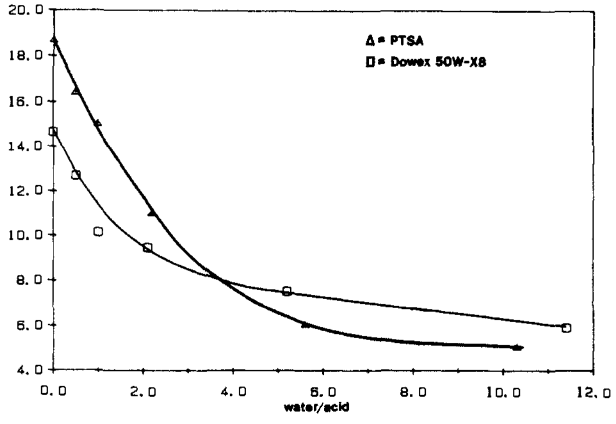

Figure 3. Heats of ionization of pyridine by PTSA and Dowex 50W-X8 in wet acetonitrile at 25 °C vs. the mole ratio water/acid.

between pyridine and the sulfonic acid moieties on the resin.

The data listed in Table VI are consistent with macroporous resins possessing rigid polymer matrices which do not collapse upon drying so that swelling is not a requirement for access to the acid sites of the polymer. The acid–base interaction between pyridine and Dowex MP-50, in the presence of at least a 10-fold excess of acid, was measurable in all eight solvents investigated, and the heat of reaction increases with the decreasing basicity of the solvent.

Naturally, the heats of reaction of pyridine with the two different resins in the various solvents of Table VI depend on the type of resin as well as the solvent. The most exothermic heats were found in hexane where solvation of the sulfonic acid groups, the pyridine, and the sulfonate anions is minimal, thus giving maximum opportunity for reaction between nearly unsolvated acid and base and the resulting anion. At the other extreme are interactions in water where all components can enjoy excellent solvation and the heat of ionization is heavily buffered by solvation of reactants as well as ions.

In view of the strong interactions with water, it is not surprising that reproducible results could only be obtained by controlling the water content of the system. A plot of the heat of ionization of pyridine by Dowex 50W-X8 and PTSA vs. water concentration is given in Figure 3 and demonstrates the influence that even relatively small amounts of water have on the energetics of this reaction. For example, the heat of ionization of pyridine with the microporous exchanger obtained when there was one water molecule per acid group was −10.15 kcal/mol, which is more than 4 kcal/mol less exothermic than the corresponding reaction under anhydrous conditions.

Comparison with Other Proton Transfer Systems. Figure 4 displays results from a preliminary study obtained by batch calorimetry in THF employing the monohydrate form of PTSA and wet Dowex 50W-X8 (Baker Laboratories) which was stored in a humidistat. The correlation between the heats of reaction of the pyridine bases with Dowex 50W-X8 and PTSA measured in wet THF are again 4 to 6 kcal/mol more exothermic for the interaction of PTSA in the presence of a large excess of acid than for the corresponding interactions in the heterogeneous system.

A reasonable correlation may be obtained between acid/base interactions in two sulfonic acid systems containing controlled but different amounts of water. Here the heterogeneous system contained about 5% (v/v) water in THF while the homogeneous system contained about 0.5% (v/v) water in THF. The meaning of the enthalpy difference between the liquid and polymeric sulfonic acid systems is difficult to interpret but certainly is related to the relative water contents of the systems.

Substituted pyridines were chosen originally as the most promising series of bases for testing the relationship between solid acids and homogeneous systems. Figure 5 compares the results gathered in this research with those obtained in several other studies with the pK_{BH^+} scale as an arbitrary standard of reference. The results for the sulfonic acid resin in acetonitrile are clearly on a par with those for the other systems.

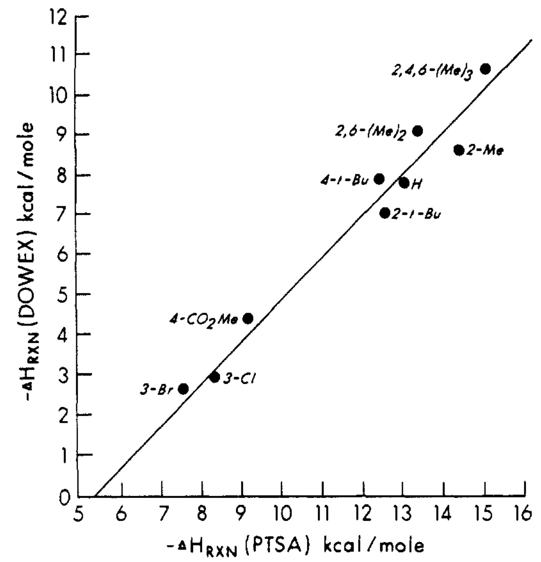

Figure 4. Heats of reaction of various substituted pyridines with Dowex 50W-X8 in wet THF by batch calorimetry at 25 °C vs. the corresponding heats of reaction with PTSA.

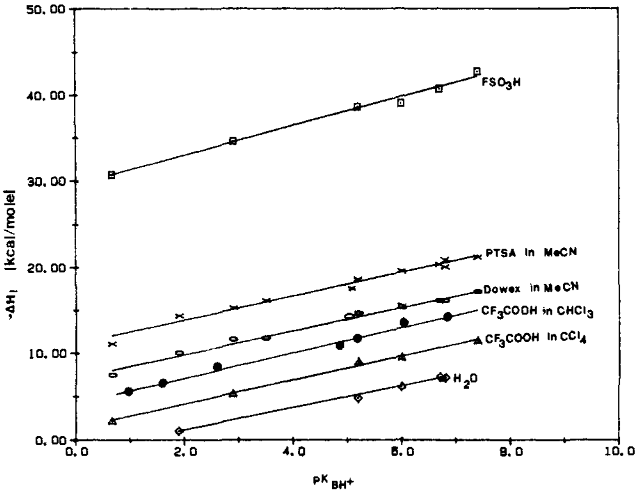

Figure 5. Heats of ionization of pyridines in various proton-transfer processes vs. pK_{BH^+} in water at 25 °C.

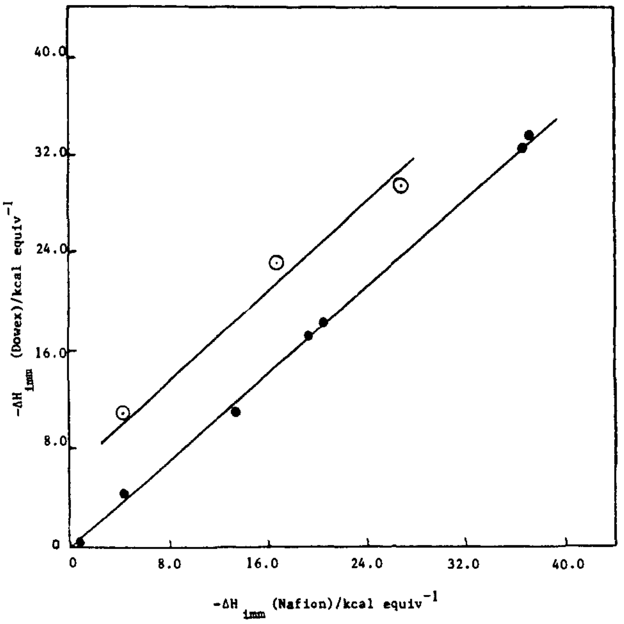

Figure 6. Heats of immersion of Dowex MP-50 and Nafion perfluorinated sulfonic acid resin in various basic liquids and water. (See Table V.)

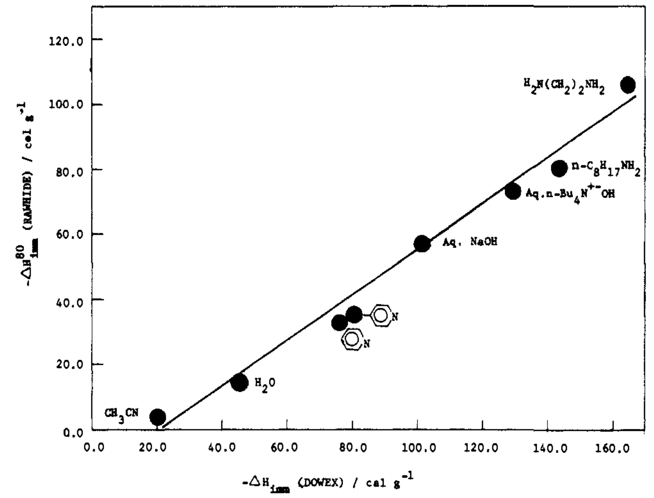

Figure 7. Heats of immersion of Dowex MP-50 at 80 °C in eight solvents vs. corresponding values for Wyoming Rawhide subbituminous coal at 80 °C.

ΔH_{rxn} vs. ΔH_{imm} for Dowex MP-50. Titration calorimetry experiments in acetonitrile and corresponding heats of immersion have been conducted with Dowex MP-50, and the results appear in Table V for the direct immersion of dry resin samples into a large excess of the various neat bases in contrast to the ΔH_{rxn} values from thermometric titrations of the bases into acetonitrile solutions or slurries of the excess acids.

A heat of immersion experiment was attempted for the interaction of microporous Dowex 50W-X8 with pyridine but gave such slow heat evolution that the reaction was incomplete even after several hours, presumably because the majority of acid sites were not accessible without prior preswelling of the polymer.

Comparison with Other Heterogeneous Systems. The heats of immersion for the sulfonic acid resin in these bases are directly relevant to the use of such measurements for comparing the distribution and types of acid sites in various kinds of solid acids. Figure 6 and Table V compares the response of Nafion, perfluorosulfonic acid resin, to that of Dowex. A clear parallel is seen between the acidic behavior of the two resins with these bases. The aqueous systems are significantly differentiated from nonaqueous ones although the slopes of the two lines are roughly parallel. Nonetheless, taking these thermochemical results at face value, Nafion is significantly stronger than Dowex as has been proposed on the basis of its catalytic behavior.

Finally, Figure 7 correlates the heats of immersion of Dowex at 80 °C in a series of bases with corresponding values for the complex natural heteropolymer, Wyoming Rawhide subbituminous coal with use of data from a previous report from this laboratory.[36] A remarkably good correlation is seen and, in contrast to Figure 6, the aqueous systems fall on the same line as the nonaqueous ones. We conclude that this sample of coal is modeled well by the purely Brönsted acid sites of Dowex sulfonic acid resin. The poor correlation between heats of immersion of Rawhide coal with Illinois No. 6 bituminous reported previously[36] suggests a different distribution of types of acid sites which we intend to discuss in future articles.

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Registry No. 3,5-Dichloropyridine, 2457-47-8; 4-cyanopyridine, 100-48-1; 3-bromopyridine, 626-55-1; 4-carbomethoxypyridine, 2459-09-8; pyridine, 110-86-1; 2-methylpyridine, 109-06-8; 3-methylpyridine, 108-99-6; 4-methylpyridine, 108-89-4; 2,6-dimethylpyridine, 108-48-5; 2,4-dimethylpyridine, 108-47-4; 2,4,6-trimethylpyridine, 108-75-8; 2,6-diethylpyridine, 935-28-4; 2,6-di-*tert*-butylpyridine, 585-48-8; 3-nitroaniline, 99-09-2; 2,6-dimethylaniline, 87-62-7; 2,4,6-trimethylaniline, 88-05-1; aniline, 62-53-3; 3,4-dimethylaniline, 95-64-7; *N*,*N*-dimethyl-3-nitroaniline, 619-31-8; *N*,*N*-dimethylaniline, 121-69-7; *N*,*N*-diethylaniline, 91-66-7; triethylamine, 121-44-8; *tert*-octylamine, 107-45-9; octylamine, 111-86-4; 1-(*N*,*N*-dimethylamino)naphthalene, 86-56-6; isopropylamine, 75-31-0; pyrrolidine, 123-75-1; quinuclidine, 100-76-5; *tert*-butylamine, 75-64-9; *p*-toluenesulfonic acid, 104-15-4; dowex 50W X8, 11119-67-8; hexylamine, 111-26-2; ethylenediamine, 107-15-3; dowex MP 50, 102807-64-7; 3-chloropyridine, 626-60-8; 2-*tert*-butylpyridine, 5944-41-2; 4-*tert*-butylpyridine, 3978-81-2.

Solvent Dependence of the Carbon Kinetic Isotope Effect on the Decarboxylation of 4-Pyridylacetic Acid. A Model for Enzymatic Decarboxylations

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Abstract: Carbon kinetic isotope effects have been measured for the decarboxylation of 4-pyridylacetic acid in pure water and in water–dioxane mixtures at 25 °C. The isotope effects are k^{12}/k^{13} = 1.064 in 75% dioxane, 1.060 in 50% dioxane, 1.056 in 25% dioxane, and 1.057 in pure water. This decrease in kinetic isotope effect parallels a more dramatic 4000-fold decrease in the observed first-order rate constant on going from 75% dioxane to pure water. No solvent isotope effect is observed in 50% water/dioxane, and as expected, the carbon isotope effect is the same in 50% D_2O/dioxane as in 50% H_2O/dioxane. The reaction appears to occur in a single step, without appreciable proton movement. The variation in rate is attributed to variations in the degree of transition-state solvation with only very small changes in ground-state effects and in the degree of carbon–carbon bond breaking in the transition state. These results indicate that the magnitudes of isotope effects observed in model reactions in H_2O are an appropriate model for magnitudes of isotope effects in enzymatic decarboxylations.

Charge neutralization is a common feature of mechanisms of enzyme-catalyzed decarboxylations.[1] In many cases, the intermediate that undergoes decarboxylation is a zwitterion involving a carboxylate connected by a conjugated system to an ammonium ion or oxonium ion. The two charges are neutralized in the decarboxylation step (eq 1). Examples include reactions de-

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(1) O'Leary, M. H. *Bioorganic Chemistry*; van Tamelen, E. E., Ed.; Academic Press: New York, 1977; Vol. 1, p 259.