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with P_4 and allows several small higher oxide species to be trapped for spectroscopic study.

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Carbon and Proton Basicity

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Abstract: Thermodynamic basicities toward protons and methyl cations in the gas phase are compared for a variety of bases. It is shown that because the heats of formation of the corresponding neutral compounds are well correlated, the proton affinities and methyl cation affinities of many of the common bases in organic chemistry are surprisingly well correlated also.

The relationship between carbon and proton basicity has been a matter of continuing interest in chemistry.[1] Examination of this relationship has provided a number of interesting insights. The most widely cited analysis is that of Hine and Weimer[2] although numerous others have been important contributions.[3-5] Prior to Hine's work, it was generally believed that "thermodynamic affinity for carbon parallels that for hydrogen".[2] Subsequent to Hine's seminal paper, the general lore associated with this problem changed and can be summarized briefly: While there appears to be a rough correlation of carbon and proton basicity, especially within a similar series of bases, there are numerous cases where the correlation is poor, and indeed attempts to predict carbon basicity from proton basicity are likely to fail. Thus, in one of the more widely cited examples,[2,5] in aqueous solution the methyl basicity of CN^- is 10^{14} greater than that of $C_6H_5O^-$, but it is 10 times less basic toward protons.

In the process of trying to analyze nucleophilic reactivity in terms of intrinsic properties of nucleophiles and the exothermicities of their reactions, we noted that the behavior of bases in the gas phase toward protons and methyl cations is not nearly as random as might be thought, based on the above example and others like it.[6] The purpose of this paper is to point out that the thermochemistry of bases toward protons and methyl cations is, in fact, very regular and that carbon basicity can be reasonably well predicted from proton basicity.

That the correlation of proton and methyl cation basicity is roughly satisfactory can be seen in Figure 1, in which the methyl cation affinity has been plotted against the proton affinity for a wide variety of common bases.[7-10] We have made use of gas-phase values because these are a rather complete set, are probably more reliable than solution values for these purposes, cover an extremely wide range, and are free of solvation effects, thus representing intrinsic molecular behavior. Inasmuch as the entropy changes for gas-phase proton-exchange reactions are either zero or very small,[11] the use of enthalpy rather than free energy is appropriate here. In fact, equilibrium acidities of acids in solution are often strongly affected by entropy changes, owing to solvation effects, vide infra. There are indeed some substantial deviations even in the gas-phase plot, and when these are converted from energy to equilibrium constants, a comparison between some pairs of bases can produce a large difference. One of the most striking pairs is CN^- and F^-. CN^- is about 10^{13} times less basic toward protons than is F^-, but about 10 times more basic toward CH_3^+. In the gas phase, CN^- is much more basic than is $C_6H_5O^-$ toward CH_3^+ but only slightly more basic toward H^+, echoing its solution behavior.

Analysis. It is tempting to analyze Figure 1 in terms of positive deviations (mostly carbon acids) and negative deviations (mostly other first-row anions). The simple plot of methyl cation affinity vs proton affinity in Figure 1 lacks an important element, however. The essence of our analysis can be seen from eq 1 and 2, which define the proton affinity (PA) and the methyl cation affinity (MCA).

$$\mathrm{HA} \rightarrow \mathrm{H}^+ + \mathrm{A}^- \qquad \mathrm{PA} = \Delta H^\circ$$

$$\mathrm{PA} = \Delta H_f^\circ(\mathrm{H}^+) + \Delta H_f^\circ(\mathrm{A}^-) - \Delta H_f^\circ(\mathrm{HA}) \tag{1}$$

$$\mathrm{CH_3A} \rightarrow \mathrm{CH_3}^+ + \mathrm{A}^- \qquad \mathrm{MCA} = \Delta H^\circ$$

$$\mathrm{MCA} = \Delta H_f^\circ(\mathrm{CH_3}^+) + \Delta H_f^\circ(\mathrm{A}^-) - \Delta H_f^\circ(\mathrm{CH_3A}) \tag{2}$$

$$\mathrm{MCA(A^-)} - \mathrm{PA(A^-)} = \Delta H_f^\circ(\mathrm{CH_3}^+) - \Delta H_f^\circ(\mathrm{H}^+) - \Delta H_f^\circ(\mathrm{CH_3A}) + \Delta H_f^\circ(\mathrm{HA}) \tag{3}$$

Since the heats of formation of H^+ and CH_3^+ are constants, one can see immediately from eq 3 that the relationship of proton affinities and methyl cation affinities depends only on the heats of formation of the corresponding neutrals HA and CH_3A and has nothing to do with the ions at all, either in solution or in the gas phase.[12] Moreover, if the differences between these heats

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[1] For example, see: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; p 367.

[2] Hine, J.; Weimer, R. D., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 3387.

[3] Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley: New York, 1975; p 225.

[4] See ref 2 and 3 for some of the relevant contributions to this area.

[5] Bordwell, F. G.; Cripe, T. A.; Hughes, D. A. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds.; Advances in Chemistry Series 215; American Chemical Society: Washington, DC, 1987; p 137.

[6] Brauman, J. I.; Dodd, J. A.; Han, C.-C. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds.; Advances in Chemistry Series 215; American Chemical Society: Washington, DC, 1987; p 23.

[7] Heats of formation of neutrals have been taken from: Benson, S. W.; *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

[8] Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, Chapter 11.

[9] Methyl cation affinities have been calculated by the proton affinities and the heats of formation of the neutral proton and methyl acids, vide infra.

[10] Hydrogen (H_2) has not been included in the least-squares regression.

[11] In general the entropy change will be identical for the proton and methyl basicity, unless the rotational degrees of freedom are different for the corresponding compounds. This will occur for atomic bases or linear bases with nonlinear conjugate acids.

[12] This has been fully understood and noted before by all of the authors who have made important contributions to the area.

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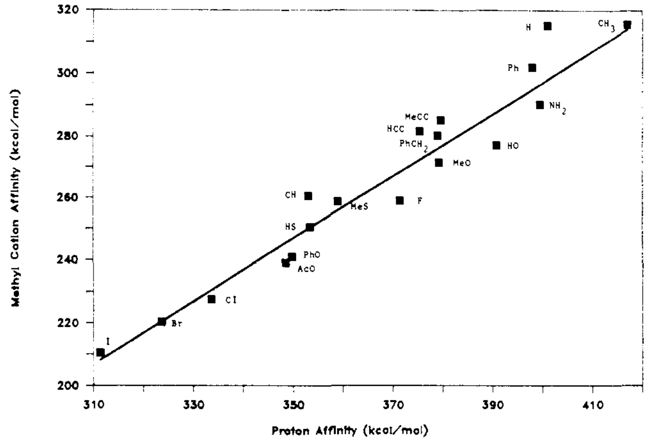

Figure 1. Proton affinities and methyl cation affinities.

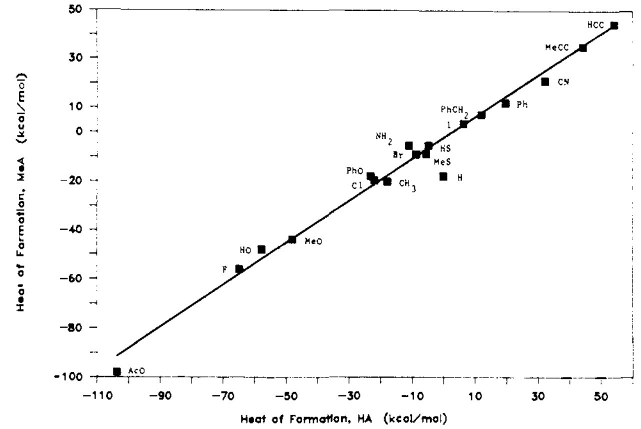

Figure 2. Heats of formation of protonated and methylated bases.

of formation, $\Delta H_f°(HA) - \Delta H_f°(CH_3A)$, were constant, then the proton affinity would correlate with the methyl cation affinity with unit slope. Equation 3 shows that unless these fundamental relationships hold, we should not expect a good correlation; indeed the correlation in Figure 1 may arise simply because $-\Delta H_f°(CH_3A) + \Delta H_f°(HA)$ is only roughly constant.

The apparent lack of correlation noted by Hine and Weimar[2] thus suggests by implication that there must not be a simple connection between the heats of formation of the neutrals. This, however, is not the case. As seen in Figure 2, the heats of formation of the proton and methyl compounds for a wide variety of bases correlate very well.[10,13] If the slope of the least-squares line were unity, then indeed proton and methyl cation affinities would be well correlated. The slope, however, is about 0.86, so eq 3 does not have a constant value for all A^-. That is, the difference between methyl cation affinity and proton affinity is not a constant. We can, however, use the plot in Figure 2 to write eq 4. Combining eq 3 and 4, we obtain eq 5. The constant includes the differences in heats of formation[14] of CH_3^+ and H^+, as well as the 2.35 kcal/mol from eq 4.

$$\Delta H_f°(CH_3A) = 0.857\Delta H_f°(HA) - 2.35 \text{ (kcal/mol)} \quad (4)$$

$$MCA(A^-) = PA(A^-) + 0.143\Delta H_f°(HA) - 101.7 \text{ (kcal/mol)} \quad (5)$$

The result of this treatment is plotted[10] in Figure 3. The plot is quite good, ranging over about 100 kcal/mol, with a correlation coefficient of 0.993. The standard deviation is about 3 kcal/mol, which is only slightly larger than the reliability of the heats of formation themselves. A statistical fit, which allows variation in the coefficient for $PA(A^-)$ and the intercept, improves the prediction slightly. The statistical fit could be improved further by also allowing the coefficient for $\Delta H_f°(HA)$ to be adjusted.

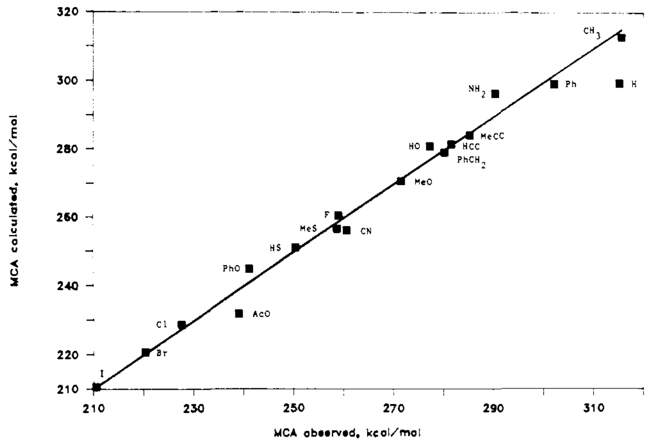

Figure 3. Calculated and observed methyl cation affinities.

Additional Considerations. The analysis presented above suggests that, generally speaking, solution behavior of proton and methyl cation affinities should also be understandable in comparable terms. Two important features, however, make the solution chemistry different.

First, the solvation energies of CH_3^+ and H^+ are very different. Thus, the absolute values of methyl cation affinities in water are much larger than the corresponding proton affinities, as compared with the gas phase in which the proton affinities are higher. This is why, for example, HCl is dissociated in water while CH_3Cl is not. These absolute differences mean that different constants will be involved in the correlation of MCA with PA, but the correlation itself is independent of the absolute values. The same argument applies to the absolute acidities of various compounds as the solvent is changed. The absolute values of acidity of the proton or methyl acids will change, but the correlation is independent of these absolute values.[15]

Second, the more interesting issue involves the relative enthalpies and free energies of solvation of the proton and methyl acids. Here, we may expect that the correlation in solution can be affected significantly if there are major differential effects on the solvation energies of the neutral compounds. Obviously, hydrogen bonding in aqueous solution will play a significant role. We would thus expect deviations when comparing, say, oxygen acids such as alcohols and phenols with carbon acids such as toluene in which hydrogen bonding is essentially unimportant. Similarly, HCl may experience a large solvent effect compared with that of CH_3Cl. Finally, as noted above, solution entropy changes are not constant, in contrast to the gas-phase values. Thus, the free energy changes in solution are rather more complicated to deal with than those in the gas phase. To the extent that these various effects change the correlations, we need to keep in mind that we are looking at solvation phenomena of neutral compounds rather than some intrinsic property of the acids and bases themselves.

A further, very important issue is the extension of this analysis to other acids of differing structure. A recent significant discovery by Bryndza, Bercaw, and their co-workers[16,17] has shown that the bond dissociation energies of a series of organometallic complexes, L_nMA (M = Pt, Ru, Th, S, Ir) correlate extremely well,[18] with unit slope, with the bond dissociation energies of HA. Thus, as

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[13] Heats of formation of neutral compounds have been taken from ref 7. Other sources are in good agreement for these compounds: McMillen, D. F., personal communication.

[14] Heats of formation of CH_3^+ and H^+ have been taken from: Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables*; NSRDS-NBS 37; National Bureau of Standards: Washington, DC, 1971.

[15] This has also been noted in the same context as the independence of the correlation on anion structure.[2]

[16] Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.

[17] Labinger, J. A.; Bercaw, J. E., submitted for publication in *Organometallics*. This paper deals with some of the issues addressed here. Bulls, A. R.; Manriquez, J. M.; Thompson, M. E.; Bercaw, J. E., submitted for publication in *Polyhedron*.

[18] In these studies, anions that can form double bonds to the metal centers show unusually high stability in their compounds, as expected.

these authors clearly point out, the proton and metal complex basicities of the wide variety of anions studied are also strongly correlated.[19]

Conclusions. The linear, nonunit slope correlation of methyl and proton acid heats of formation speaks to a fundamental aspect of chemical bonding. A plot with some nonzero intercept and unit slope is consistent with bond additivity. We know that such correlations are often acceptable but can usually be improved by using group additivity.[20] The plot in Figure 2 shows that the group corrections in this case are functionally related. That is, the methyl compounds are intrinsically less sensitive to the nature of A than are the H compounds. Using a simple one-electron picture to describe bonding in simple acids,[21] we can write that the stabilization energy, SE, with respect to the separated orbitals of A and the acid moiety is given by eq 6 where Δ is the difference

$$\mathrm{SE} = (\Delta^2 + 4V^2)^{1/2} \qquad (6)$$

in orbital energies of A and the corresponding acid moiety (H, CH_3, etc.) and V is the strength of the perturbative interaction. The relative stability of the separated H vs methyl orbitals contributes to the constant (intercept) difference. The methyl compound stabilities are less structure sensitive than are the protonated bases, possibly because methyl can respond better in less favorable overlap situations, owing to its larger number of available orbitals. Generally speaking, the slope of such heat of formation plots will depend on the specific acid moieties involved. The observation of unit slope[16,17] in the metal cation plot suggests, therefore, that the relative perturbative interactions are similar for H and the metal cations. The full implication of these correlations is not yet clear, but the regular behavior observed by us and by Bryndza and Bercaw suggests that it may not be necessary to invoke second-order effects in order to rationalize and understand acid and base behavior for systems with rather wide variation in structure.

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Registry No. O_2, 7782-44-7; N_2, 7727-37-9; methyl cation(1+), 14531-53-4.

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[19] For some important insights into M–H and M–R bond energies, see also: Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238; *Inorg. Chim. Acta* **1985**, *100*, 41.

[20] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

[21] Brauman, J. I.; Eyler, J. R.; Blair, L. K.; White, M. J.; Comisarow, M. B.; Smyth, K. C. *J. Am. Chem. Soc.* **1971**, *93*, 6360.

Diels–Alder Reactions in Nonaqueous Polar Solvents. Kinetic Effects of Chaotropic and Antichaotropic Agents and of β-Cyclodextrin

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Abstract: The Diels–Alder addition reactions of nitrosobenzene with 1,3-cyclohexadiene and of methyl vinyl ketone with 1,3-cyclopentadiene are faster in formamide or in ethylene glycol than in other organic solvents, but not as fast as in water solution. The reactions in these organic solvents are also accelerated by β-cyclodextrin. The kinetic results indicate that there is solvophobic binding of the reactants to each other, or into the cyclodextrin cavity, in these polar solvents. In spite of this, there is no striking increase in endo/exo selectivity, as there is in water. We detect two classes of chaotropic agents. Urea and guanidinium ion, which are normally chaotropic in water and thus decrease the hydrophobic effect and the rate of our Diels–Alder reactions, show no such effect in the organic solvents. These solutes also *decrease* the solubility of benzene in ethylene glycol or in formamide, in contrast to their effects in water. The contrasts indicate that "waterlike" organic solvents still do not share some of the most striking properties of water itself. The results also indicate that the chaotropic effects of urea and of guanidinium ion in water reflect primarily the interaction of the chaotropes with the water, not with the hydrocarbon solutes. By contrast, tetramethylammonium bromide, and even more so tetrabutylammonium bromide, belong to a second class of salting-in agents. They decrease the rate of the Diels–Alder addition of cyclopentadiene to methyl vinyl ketone, and tetramethylammonium bromide increases the solubility of benzene in ethylene glycol and formamide (as it does in water). These tetraalkylammonium cations probably act as pseudodetergents and interact primarily with the solutes, not the solvents.

We have described the remarkable acceleration of Diels–Alder reactions when water is the solvent[1] and the striking increase in stereoselectivity that is seen in some cases.[2,3] The reaction rate of 1,3-cyclopentadiene with methyl vinyl ketone (reaction 1) and with acrylonitrile (reaction 2) was increased by factors of 740 and 30, respectively, when the addition was performed in water rather than in isooctane, and the reaction rate for the addition of *N*-ethylmaleimide to anthracene-9-carbinol (reaction 3) was increased by a factor of 28.

This solvent effect was principally due to the hydrophobic packing of the diene and dienophile, not to a simple polarity effect. As one piece of evidence, the rate of reaction 1 increased by only 12-fold on changing from isooctane to methanol solvent, while that of reaction 2 increased by only 2-fold with the same solvent change.[1] The large discontinuous increase in water is well above any expected polarity effect. Even more striking, in reaction 3 the rate actually *decreases* by a factor of 2.3 when methanol solvent is used instead of isooctane. In reaction 3 the hydrophobic

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[1] Breslow, R.; Rideout, D. *J. Am. Chem. Soc.* **1980**, *102*, 7816.

[2] Breslow, R.; Maitra, U.; Rideout, D. *Tetrahedron Lett.* **1983**, *24*, 1901.

[3] Breslow, R.; Maitra, U. *Tetrahedron Lett.* **1984**, *25*, 1239.

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