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## Accurate Relative Acidities in the Gas Phase. Hydrogen Sulfide and Hydrogen Cyanide[1]

*Sir:*

Solution studies of acid-base equilibria have elucidated a number of structural and electronic effects which influence the acid strength of molecules. It is well known, though, that the nature of the solvent can also have a significant effect on acidity.[2] This phenomenon has been demonstrated in a striking manner recently by studies which have shown that the acid strength of molecules in the gas phase is often quite different from that observed in solution.[3,4] For example, Brauman and Blair have reported that in the gas phase toluene is a stronger acid than water and *tert*-butoxide is less basic than methoxide.[3b] Since ions are not solvated at the low pressures used in these gas-phase experiments, the intrinsic acidity of molecules can be determined in the absence of solvent effects.

Using conventional ion cyclotron resonance (icr) techniques, Brauman and Blair were able to determine relative orders of gas-phase acidity. In this communication we demonstrate that similar systems can be studied in a quantitative manner using the pulsed icr equilibrium technique. The equilibrium constant for the gas-phase reaction

$$\mathrm{SH^- + HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CN^- + H_2S} \qquad (1)$$

is measured for the first time, and special efforts are made to demonstrate that equilibrium is being attained in this system. Equilibrium icr techniques were first used by Bowers, Aue, Webb, and McIver to determine accurate relative proton affinities for a series of amines, and a significant advantage of this new method is that thermochemical values can be measured to an accuracy of ±0.2 kcal/mol, almost an order of magnitude more accurate than previously available values.[5]

The pulsed icr technique has been described previously.[6] Gaseous ions are formed by a short pulse of an electron beam and then trapped in an analyzer cell by the combined effects of magnetic and electrostatic fields. The ions can be trapped efficiently for periods as long as 1 sec, and at any time during the trapping period the ions present in the analyzer cell can be mass analyzed.

Figure 1 shows typical experimental data used to determine the relative gas-phase acidity of $H_2S$ and HCN. One of the dual sample inlets on the pulsed icr spectrometer was used to add an $H_2S$–HCN mixture of known composition to a pressure of $1 \times 10^{-6}$ Torr, while the other inlet was used to add $NF_3$ to a total pressure of $2 \times 10^{-6}$ Torr. Fluoride ion is formed efficiently from $NF_3$ by low-energy electron impact: $NF_3 + e^- \rightarrow F^- + NF_2\cdot$.

The upper trace in Figure 1 shows that a 5-msec pulse of the electron beam produces a large initial concentration of $F^-$ which decays exponentially as it reacts with $H_2S$ and HCN. The $F^-$ rapidly abstracts a proton from $H_2S$ and HCN because it is a stronger base than $SH^-$ or $CN^-$. The middle trace in Figure 1 shows that the $CN^-$ concentration increases gradually and then levels off to a constant value after about 200 msec. The $SH^-$ concentration rises rapidly with a peak at 50 msec and then decays gradually to a constant equilibrium value.

An examination of the traces in Figure 1 suggests that equilibrium is being attained in the $H_2S$–HCN system. The reactants do reach constant concentrations after reacting for 300 msec, and the concentration of $SH^-$ first increases and then decreases as if the reverse reaction were occurring to bring the system back to equilibrium. Experiments of this type give $K = 9.0 \pm 0.6$ for the equilibrium constant of reaction 1.[7] Additional experiments were performed, however, to test further whether equilibrium is in fact being attained.

The traces labeled A in Figure 2 were obtained in the same manner as the ones in Figure 1 except that an $H_2S$–HCN mixture of different relative composition was used. The equilibrium concentration of the ions gives $K = 9.1$, in good agreement with the result obtained above. The equilibrium constant can also be determined by measuring the rate constants, $k_1$ and $k_2$, for the forward and reverse reactions: $K = k_1/k_2$. Ejection of either $CN^-$ or $SH^-$ from the analyzer cell using strong double-resonance irradiation[8] perturbs the system, and the rate at which the system responds to the perturbation is determined by the rate of the forward or reverse reaction.[9] Trace B in the upper half of Figure 2 shows that the concentration of $CN^-$ is significantly altered when $SH^-$ is totally ejected from

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(7) $K = (I_{CN^-}/I_{SH^-})(26/33)([H_2S]/[HCN])$, where $I_{CN^-}$ is the intensity of the $CN^-$ signal; 26 the mass of $CN^-$, a mass correction factor; and [HCN] the pressure of HCN in the system.

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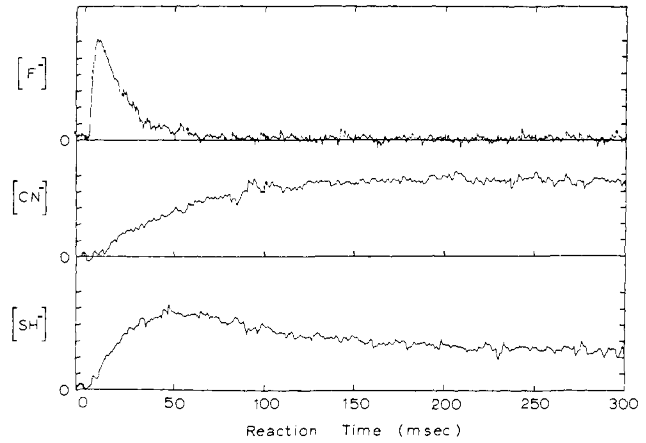

Figure 1. Pulsed icr spectra showing the concentration of F⁻ (upper trace), CN⁻ (middle trace), and SH⁻ (lower trace) as a function of reaction time for a 3.98 : 1.00 mixture of $H_2S$:HCN.

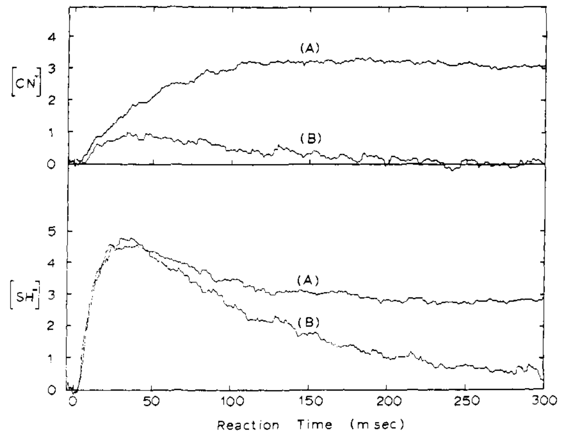

Figure 2. Pulsed icr spectra for a 10.41 : 1.00 mixture of $H_2S$ and HCN. Upper half: (A) concentration of CN⁻ *vs.* reaction time, (B) concentration of CN⁻ *vs.* reaction time when SH⁻ is ejected from the cell. Lower half: (A) concentration of SH⁻ *vs.* reaction time, (B) concentration of SH⁻ *vs.* reaction time when CN⁻ is ejected from the cell.

the icr analyzer cell, and trace B in the lower half of Figure 2 shows the analogous situation when the concentration of SH⁻ is monitored and CN⁻ is ejected continuously. If CN⁻ and SH⁻ were not chemically coupled, then ejection of one of them would have no effect on the other. A more detailed kinetic analysis[9] shows that this method for measuring the rate of the forward and reverse reactions gives $K = k_1/k_2 = 8.9 \pm 0.5$.

$NF_3$ was used in the experiments described above because it is a convenient and efficient source of negative ions in the gas phase. However, experiments have also been performed with binary mixtures of $H_2S$ and HCN. SH⁻ formed directly at 6 eV (uncorrected) by dissociative electron attachment to $H_2S$ serves as the source of negative ions. Formation of the negative ions by a different primary mechanism is another means of testing whether thermal equilibrium is being attained. These experiments are more difficult than the ones using $NF_3$, but still $K = 10.1 \pm 1.8$ was obtained. The two different modes of negative ion formation are likely to give rise to different initial internal energies in the ions studied, yet values of $K$ are obtained which agree within experimental error.

The excellent agreement among equilibrium constants obtained by three different methods supports our contention that thermal equilibrium is closely approached in the pulsed icr experiments. Furthermore, using the average value $K = 9.5 \pm 1.5$ for reaction 1, a value of $\Delta H_f^{298}(CN^-) = 15.5 \pm 1.3$ kcal/mol can be calculated from existing thermochemical data.[10] This is in quite good agreement with $\Delta H_f^{298}(CN^-) = 15 \pm 1.5$ kcal/mol which can be derived from the photoionization measurements of Berkowitz, Chupka, and Walter.[11]

The ability to measure gas-phase ionic equilibria shows great promise for the determination of accurate relative stabilities of positive and negative gaseous ions. The measurement of equilibrium constants for proton transfer reactions such as reaction 1 will permit establishment of an absolute gas phase acidity scale. Such a scale is not only of inherent interest, but also will allow determination or reconfirmation of many bond strengths and electron affinities.[12]

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[10] Obtained using $\Delta G = -RT \ln K$, $\Delta H = \Delta G + T\Delta S$; $T = 298$°K; $\Delta S = 2.7$ eu calculated from $S_0^{298}$ values for HCN, $H_2S$, and the *radicals* SH· and CN· in S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, pp 196–198; $\Delta H_f^{298}(H_2S) = 4.9$ kcal/mol, $\Delta H_f^{298}(HCN) = 32.3$ kcal/mol from D. D. Wagman, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards (U. S.) Technical Note No. 270-3, 1968; the $D_0(HS\text{–}H) = 89.3 \pm 0.7$ kcal/mol value from V. H. Dibeler and S. K. Liston, *J. Chem. Phys.*, **49**, 482 (1968); and the electron affinity of HS· = 53.5 kcal/mol from B. Steiner, *ibid.*, **49**, 5097 (1968).

[11] Obtained using an estimated threshold of 819 ± 2 Å at 298°K for the process $h\nu + HCN \rightarrow H^+ + CN^-$ from J. Berkowitz, W. A. Chupka, and T. A. Walter, *ibid.*, **50**, 1497 (1969); $\Delta H_f^{298}(H^+) = 365.7$ kcal/mol; and $\Delta H_f^{298}(HCN) = 32.3$ kcal/mol as in ref 10.

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## Electron Paramagnetic Resonance of 9,9′-Dianthrylmethylene. A Linear Aromatic Ground-State Triplet Methylene

*Sir:*

An aromatic ring adjacent to a divalent carbon usually does not affect the angle at that site. Methylene,[1,2] phenylmethylene,[3] diphenylmethylene,[3–5] 1- and 2-naphthylmethylenes,[6] and 9-anthrylmethylene[6] have ap-

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