have been observed in $[Mn(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]^{n+}$ ($n = 1, 2$).[20] The lengthening of the Fe–P bonds as the metal oxidation state increases is probably due to the decreasing Fe–P orbital overlap as the metal orbitals contract. Correspondingly, the shortening of the Fe–Cl bonds **1** < **2** < **3** reflects a stronger interaction with the σ and π donor orbitals of the chloride as the charge on the metal increases. Furthermore, it has been pointed out[28] that, for Fe(II) with the $(t_{2g})^6$, configuration there may be a destabilizing π-repulsion between the chlorine $p\pi$ and the filled metal acceptor orbitals which will decrease as the t_{2g} orbitals are progressively emptied. The strong axial compression observed in **3** by EXAFS also correlates well with the results of ^{57}Fe Mössbauer studies on the diarsine analogue, which concluded[21] that the complex possessed a $^3A_2$ ground state with a strengthening of the ligand field along the Cl–Fe–Cl axis compared with the Fe(II) and Fe(III) systems.

Acknowledgment. We thank the SERC for postgraduate studentships (S.K.H. and S.J.H.) and for provision of funds to establish the EXAFS service. The Director of the Daresbury Laboratory is thanked for the provision of facilities.

C–Xe Bond Strength in the Methylxenonium Cation Determined from Ion Cyclotron Resonance Methyl Cation Exchange Equilibria

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Since the original discovery by Bartlett[1] of a species containing a XeF bond, a variety of other xenon-containing compounds have been prepared and characterized. Both ionic and covalent bond compounds have been synthesized involving bonds between xenon and boron,[2] fluorine,[3] nitrogen,[4] and oxygen.[5] In addition evidence has been presented for a C–Xe bond in $(CF_3)_2Xe$[6] and transient XeCl has been used in excimer lasers.[7] Despite the variety and number of xenon-containing compounds, however, very little quantitative information is available for bond dissociation energies of bonds to xenon. Very early kinetic experiments by Johnston[8] established Xe–F bond strengths in XeF_4, XeF_2, and XeF of 48, 54, and 11 kcal mol^{-1}, respectively. Later photoionization mass spectrometric appearance energy measurements were used to accurately determine $\Delta H_f°(XeF_2)$,[9] and a value for the Xe–F bond energy in XeF_2 of 55 kcal mol^{-1} was obtained.

Holtz and Beauchamp[10] have carried out ion-molecule reactions in H_2, Xe, and CH_3F mixtures in an ICR spectrometer and have observed eq 1, which establishes the methyl cation binding energy

$$CH_3FH^+ + Xe \rightarrow XeCH_3^+ + HF \qquad (1)$$

of Xe as greater than that of HF. On the basis of failure to observe the analogous reaction for CH_3ClH^+ (and the accepted thermochemical data at the time) a methyl cation binding energy for Xe of 43 ± 8 kcal mol^{-1} was deduced.

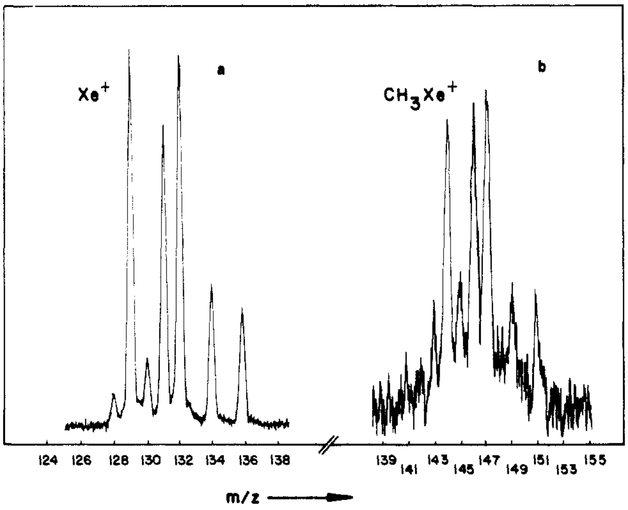

Figure 1. (a) Partial mass spectrum of Xe at a total pressure of 10^{-6} torr and 70-eV electron energy. (b) Time-delayed mass spectrum of the m/z 140–156 region for an 18:1 mixture of Xe/CH_3F at a total pressure of 2×10^{-6} torr, 200 ms following a 5-ms, 70-eV electron beam pulse.

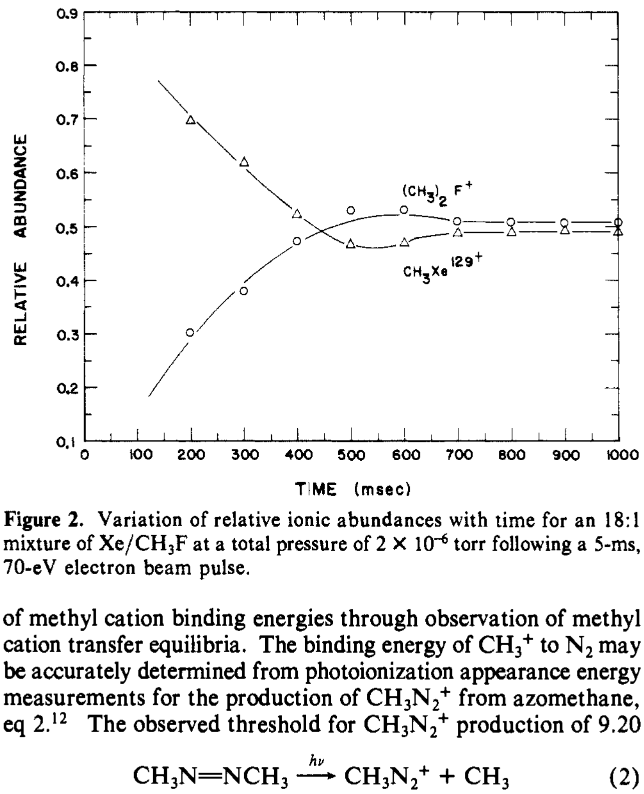

Figure 2. Variation of relative ionic abundances with time for an 18:1 mixture of Xe/CH_3F at a total pressure of 2×10^{-6} torr following a 5-ms, 70-eV electron beam pulse.

Recently a pulsed electron beam high-pressure mass spectrometric method[11] has been developed for the accurate determination of methyl cation binding energies through observation of methyl cation transfer equilibria. The binding energy of CH_3^+ to N_2 may be accurately determined from photoionization appearance energy measurements for the production of $CH_3N_2^+$ from azomethane, eq 2.[12] The observed threshold for $CH_3N_2^+$ production of 9.20

$$CH_3N{=}NCH_3 \xrightarrow{h\nu} CH_3N_2^+ + CH_3 \qquad (2)$$

± 0.03 eV and standard neutral thermochemistry[13] allow calculation of the methyl cation affinity of N_2 as 51.9 ± 1.7 kcal mol^{-1}. In the high-pressure mass spectrometer an ion-molecule reaction sequence, eq 3–5, in N_2–CH_3F mixtures in which N_2 is present

$$N_2^+ + CH_3F \rightarrow CH_3F^+ + N_2 \qquad (3)$$

$$CH_3F^+ + CH_3F \rightarrow CH_3FH^+ + CH_2F \qquad (4)$$

$$CH_3FH^+ + N_2 \rightarrow CH_3N_2^+ + HF \qquad (5)$$

$$CH_3N_2^+ + CH_3F \rightleftharpoons (CH_3)_2F^+ + N_2 \qquad (6)$$

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in large excess, leads to the production of dimethylfluoronium ion, $CH_3FCH_3^+$. Subsequent methyl cation transfer equilibrium, eq 6, establishes the methyl cation affinity of CH_3F as 59.2 ± 2.0 kcal mol^{-1}.[11]

This accurate determination of the methyl cation affinity of CH_3F has subsequently been used in this laboratory to provide a reference point for determination of further methyl cation affinities by ion cyclotron resonance spectroscopic observation of methyl cation transfer equilibria involving CH_3F, eq 7.[14] Included

$$(CH_3)_2F^+ + B \rightleftharpoons CH_3B^+ + CH_3F \qquad (7)$$

in these experiments is the observation of methyl cation transfer equilibria involving CH_3F and Xe, eq 8, which may be used to

$$(CH_3)_2F^+ + Xe \rightleftharpoons CH_3Xe^+ + CH_3F_3 \qquad (8)$$

determine the methyl cation binding energy to Xe. Verification that the species observed is in fact CH_3Xe^+ may be seen in Figure 1 where identical isotopic distributions for Xe^+ and CH_3Xe^+ are shown. A typical methyl cation transfer equilibrium between CH_3F and Xe is illustrated in Figure 2.

In order to unambiguously ascertain the value of the equilibrium constant for eq 8, K_8, several replicate experiments were carried out in which the CH_3F:Xe pressure ratio was varied by a factor of 3. The data obtained from these equilibrium observations yield a value for K_8 of 0.16 ± 0.05 which allows a value of $\Delta G_8°$ of 1.1 ± 0.2 kcal mol^{-1} to be calculated. The low pressures involved in ICR experiments preclude determination of the entropy change, $\Delta S_8°$, by examination of the temperature dependence of K_8. However, it has been shown in the past that absolute entropies of ions may be reliably estimated from known entropies of isoelectronic neutrals.[15] Thus $S°((CH_3)_2F^+)$ may be estimated as 63.7 cal mol^{-1} K^{-1} from the experimental value for $(CH_3)_2O$ and $S°(CH_3Xe^+)$ may be estimated to be 60.5 cal mol^{-1} K^{-1} from data for CH_3I.[16] The maximum uncertainty in the ionic entropy estimates is probably ±0.5 cal mol^{-1} K^{-1}. These estimates and known entropy data for Xe and CH_3F establish $\Delta S_8°$ as 9.6 ± 1.0 cal mol^{-1} K^{-1}. Combining this entropy data with the value of $\Delta G_8°$ measured at ambient temperature (298 K) which gives the enthalpy change, $\Delta H_8°$, as 4.0 ± 0.5 kcal mol^{-1} allows a calculation of the methyl cation affinity of Xe of 55.2 ± 2.5 kcal mol^{-1}.

It is interesting to note the relative proton affinities and methyl cation affinities of Xe and a variety of other weak bases. For example equilibrium measurements establish the methyl cation affinity of Xe as 1.5 kcal mol^{-1} less than that of N_2O and 1.4 kcal mol^{-1} greater than that of CO_2.[11] This order is different than the order of proton affinities for these compounds in which Xe is found to be a weaker base than CO_2.[17] The principle attractive interactions in CH_3^+ adducts with weak bases will be electrostatic (ion-induced dipole) and covalent while the interaction in H^+ adducts will be much more predominantly covalent. The reversal in basicities of Xe and CO_2 toward H^+ and CH_3^+ may then be understood in terms of the increased relative importance of the electrostatic component of interaction in CH_3^+–Xe due to the much greater polarizability of Xe (4.02 Å^3) relative to CO_2 (2.59 Å^3). It should be noted, however, that the covalent component of interaction in CH_3–Xe^+ must still be appreciable.[18]

In summary, a method for establishing CH_3^+ binding energetics has been presented and applied to Xe to give a C–Xe bond strength of 55.2 ± 2.5 kcal mol^{-1} in CH_3Xe^+. Recent efforts in this laboratory have resulted in generation of CH_3Kr^+ and initial evidence indicates that a C–Kr bond strength in this ion may also be obtainable.[19] These data lead to the suggestion that CH_3Xe^+ and CH_3Kr^+ may be observable in CH_3F, SbF_5, and Xe or Kr mixtures by NMR.[20]

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Registry No. $XeCH_3^+$, 34176-86-8; CH_2N_2, 20404-06-2; CH_3F, 593-53-3; $(CH_3)_2F^+$, 64710-12-9; N_2, 7727-37-9.

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(14) All experiments were carried out at 298 K using an ion cyclotron resonance spectrometer of basic Varian V-5900 design, extensively modified to permit operation in both conventional drift and trapped ion modes. Both marginal oscillator and capacitance bridge detection systems were used in these experiments. Accurate partial pressure ratios of Xe and CH_3F were obtained with a Validyne capacitance manometer. Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

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One-Step Synthesis of a 9-Phosphabarbaralane. Close Approach to a Bishomoaromatic System in the Solid State

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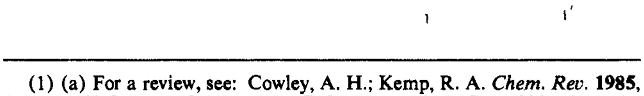
Phosphenium ions (R_2P^+) exhibit an interesting and diversified reactivity[1] and have been recently reported to undergo 1,4-addition to 1,3-dienes to yield 3-phospholenium ions.[1b,c] We now report the following: (i) the addition of a phosphenium ion to cyclooctatetraene to effect a one-step synthesis of a 9-phosphabarbaralane (**1**), (ii) the first structural information on a heteroatom-substituted barbaralane, and (iii) a solid-state structure closely approaching the geometry of the transition state for a Cope rearrangement.

Cyclooctatetraene (10.8 mmol, about 5M in CH_2Cl_2) is added dropwise to a stirred solution of $[(Me_2N)(Cl)P][AlCl_4]$[2] (10.8 mmol, about 0.5 M in CH_2Cl_2) cooled by an ice-water bath. The ice is allowed to melt and the reaction mixture warmed to room temperature. The reaction is monitored by ^{31}P NMR spectroscopy and after about 3 h appears to be complete with only one signal observed (80.8 ppm). The solvent is removed and the crude solid recrystallized by allowing heptane to diffuse into a methylene chloride solution at −35 °C. The product, **1**, is a colorless solid (mp dec 262 °C).[3]



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