solvent coordinated CH_3CN was displaced yielding the THF adduct $[Cp_2Zr(CH_3)(THF)][BPh_4]$ (**2**-BPh_4) which was isolated as a pale yellow crystalline solid.[16] **1**-BPh_4 also formed stable complexes with the hard unhindered Lewis bases 4,4′-dimethylbipyridine and 4-(dimethylamino)pyridine in CH_3CN but not with PPh_3 or diphos.[17]

As expected for Cp_2Zr^{IV} complexes lacking π donor ligands,[18] **1** and **2** reacted rapidly with CO in CH_3CN to produce (in the BPh_4^- cases) $[Cp_2Zr(COCH_3)(CH_3CN)][BPh_4]$ (**3**-BPh_4) isolated (70%) as a yellow solid.[19] Unlike neutral Cp_2Zr^{IV} acyl complexes, **3**-BPh_4 and its THF and PF_6^- analogues did not release CO under vacuum.[20] Also, unlike neutral Cp_2Zr^{IV} alkyl complexes,[21,22] the cationic zirconium alkyls **1** and **2** add rapidly to ketones under mild conditions. For example, **1**-BPh_4 reacted with benzophenone at room temperature in THF (ca. 1 h) to produce $[Cp_2Zr(OCPh_2CH_3)(THF)][BPh_4]$ (**4**) (100% by ^1H NMR).[23] When this reaction was monitored by ^1H NMR spectroscopy, transient signals (δ 6.22 (s, 10 H), 0.47 (s, 3 H)) presumably due to an intermediate adduct $[Cp_2Zr(CH_3)(OCPh_2)][BPh_4]$ were observed. In contrast, $Cp_2Zr(CH_3)_2$ reacted only extremely slowly with benzophenone (30% complete after 70 h, 110 °C, sealed tube) to produce $Cp_2Zr(CH_3)(OCPh_2CH_3)$.

The observed F^- abstraction from PF_6^-, the selectivity for adduct formation with Lewis bases, and the reactivity with CO and carbonyl compounds characterize the fragment $Cp_2ZrCH_3^+$ as a highly electrophilic hard Lewis acid. We are currently exploring the reactivity of **1**–**3**, and other cationic Cp_2Zr^{IV} complexes, with olefins, acetylenes, and other substrates.[24]

Acknowledgment. Support from the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Washington State University Research and Arts Committee is gratefully acknowledged.

Registry No. **1**-PF_6, 100909-46-4; **1**-BPh_4, 100909-48-6; **2**-BPh_4, 100909-50-0; **3**-BPh_4, 100909-54-4; **4**, 100909-56-6; $Cp_2Zr(CH_3)Cl$, 1291-45-8; $Cp_2Zr(CH_3)I$, 63643-49-2; $Cp_2Zr(CH_3)F$, 100909-47-5; Cp_2ZrF_2. 11090-85-0; $Cp_2Zr(CH_3)_2$, 12636-72-5; $Cp_2Zr(CH_3)(OCPh_2CH_3)$, 100909-57-7; $[Cp_2Zr(CH_3)(4,4'\text{-dimethylbipyridine})][BPh_4]$, 100909-52-2; benzophenone, 119-61-9.

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(16) **2**-BPh_4: ^1H NMR (CD_2Cl_2) δ 7.6–6.7 (m, 20 H, BPh_4^-) 6.31 (s, 10 H), 3.44 (m, 4 H, THF), 1.80 (m, 4 H, THF), 0.74 (s, 3 H). The absorbances due to coordinated THF are shifted 0.23 and 0.01 δ upfield from those of free THF (3.67, 1.81) in this solvent. Anal. Calcd: C, 74.62; H, 6.58, Zr, 14.53. Found: C, 74.51, H, 6.63, Zr, 14.52.

(17) $[Cp_2Zr(CH_3)(4,4'\text{-dimethylbipyridine})][BPh_4]$: Isolated as the toluene solvate by recrystallization from CH_3CN/toluene. Anal. Calcd for $C_{54}H_{53}N_2BZr$: C, 77.95; H, 6.42; N, 3.37. Found C, 77.75; H, 6.34; N, 3.56. ^1H NMR (CD_3CN) δ 8.70 (d, 7 Hz, 1 H), 8.49 (d, 6 Hz, 1 H), 8.19 (s, br, 2 H), 7.54 (d, 7 Hz, 1H), 7.4–6.6 (m, 21 H, BPh_4^- and bpy) 5.93 (s, 10 H), 2.56 (s, 3 H), 2.51 (s, 3 H), 0.43 (s, 3 H, $ZrCH_3$); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 165 (q, $J_{^{13}C-^{11}B}$ = 49.5 Hz), 156.0, 155.1, 154.4, 152.9, 152.8, 152.0, 137.0, 128.0, 125.9, 122.0, 112.4, (Cp_2Zr), 35.9 ($ZrCH_3$, $J_{^{13}C-^1H}$ = 121 Hz from gated decoupled spectrum), 21.7.

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(19) **3**-BPh_4: ^1H NMR (CD_3CN) δ 7.4–6.7 (m, 20 H, BPh_4^-) 6.00 (s, 10 H), 3.06 (s, 3 H), 1.95 (s, 3 H); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 315.0 ($ZrCOCH_3$), 164.6 (q, $J_{^{13}C-^{11}B}$ = 49.5 Hz), 136.6, 126.5, 122.6, 110.6 (Cp_2Zr), 33.8 (CH_3); IR ν_{CN} 2304, 2276 cm^{-1}, ν_{CO} 1563 cm^{-1}. Anal. Calcd: C, 73.06; H, 5.81; N, 2.24; B, 1.73; Zr, 14.60. Found: C, 72.78; H, 5.98; N, 2.49; B, 1.90; Zr, 14.36.

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(23) **4**: ^1H NMR (CD_3CN) δ 7.5–6.7 (m, 30 H), 6.32 (s, 10 H), 3.65 (m, 4 H), 1.95 ($OCCH_3$, masked by solvent peak), 1.80 (m, 4 H); ^1H NMR (THF-d_8) δ 7.5–6.7 (m, 30 H), 6.28 (s, 10 H), 1.93 (s, 3 H); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 164 (q, $J_{^{13}C-^{11}B}$ = 50 Hz), 148.5, 136.4, 128.8, 127.7, 126.3, 122.4, 115.4, 88.4 ($ZrOCPh_2CH_3$), 68.1 (THF), 31.5, 26.1 (THF).

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(25) In this paper the periodic group notation in parentheses is in accord with recent reactions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Deuterium Fractionation Factor for the Gas-Phase Hydronium Ion

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The hydronium ion, L_3O^+ where L = D or H, plays a central role in the interpretation of isotope effects in aqueous solutions. Several workers[1-5] have measured the isotope effect for the hydronium ion in deuterated aqueous solutions which may be expressed in terms of the equilibrium constant for reaction 1, K_1

$$2H_3O^+(l) + 3D_2O(l) \rightleftharpoons 3H_2O(l) + 2D_3O^+(l) \qquad (1)$$

= 0.11. More commonly, however, the isotope effect is reported in terms of a fractionation factor,[6,7] ϕ_1, that expresses, on a per hydrogen basis with statistical effects removed, the effect of the change in environment in proceeding from bulk solvent to solvated solute. The fractionation factor for the hydronium ion is equal to $(K_1)^{1/6}$ and has a value of 0.69 ± 0.02. This value indicates that, relative to water protium is accumulating in the hydronium ion and therefore the force field for O–H bonds in the hydronium ion is weaker than in water. Both the positive charge and the hydrogen bonding of the hydronium ion to solvent water, as indicated in the formula $O(L\text{---}OL_2)_3^+$, could contribute to this weakening of the proton bond.[7-9] Recently, Kurz et al.[10] have investigated the relative importance of these two factors by measuring the fractionation factor of hydronium ion in acetonitrile. They obtained a fractionation factor of 0.79 for this *unhydrated hydronium ion* and concluded that either hydrogen bonding is of secondary importance in influencing the fractionation factor or that the hydrogen bonding from L_3O^+ to $NCCH_3$ is almost as effective in weakening the force field as is the hydrogen bonding in the aqueous system. The value of the fractionation factor for the completely unsolvated, gaseous hydronium ion should provide considerable insight into this question. The statistical mechanical calculations of Henchman, Smith, and Adams[11] contain estimates that lead to a fractionation factor for gaseous L_3O^+ with a large uncertainty. In the present paper we report the first accurate experimental determination of the fractionation factor for the hydronium ion in the gas phase.

A mixture of $H_2O(l)$ and $D_2O(l)$ was made up by weight and placed in a large glass bulb. The partial pressures of $H_2O(g)$,

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Table I. Distribution of L_3O^+ Ions in Equilibrium with $D_2O/H_2O/HOD$ Mixtures at 25 °C

mixture 1: $X_{H_2O(l)}{}^a = 0.498$; $X_{H_2O(g)}{}^b = 0.268$; $X_{HOD(g)} = 0.493$; $X_{D_2O(g)} = 0.239$			mixture 2: $X_{H_2O(l)} = 0.493$; $X_{H_2O(g)} = 0.263$; $X_{DOH(g)} = 0.495$; $X_{D_2O(g)} = 0.243$		
species	mass	ion fraction	species	mass	ion fraction
H_3O^+	19	$0.20_9 \pm 0.02_5$	H_3O^+	19	$0.18_7 \pm 0.01_7$
DH_2O^+	20	$0.38_1 \pm 0.01_0$	DH_2O^+	20	$0.38_4 \pm 0.00_4$
D_2HO^+	21	$0.30_7 \pm 0.01_7$	D_2HO^+	21	$0.32_0 \pm 0.00_9$
D_3O^+	22	$0.09_6 \pm 0.01_1$	D_3O^+	22	$0.11_4 \pm 0.02_0$

[a] Directly from weights of $D_2O(l)$; $H_2O(l)$. [b] Calculated from $X_{H_2O(l)}$.

HDO(g), and $D_2O(g)$ in the vapor above this liquid mixture were calculated from data given in the literature.[12] The inlet system of the ion cyclotron resonance (ICR) spectrometer was conditioned by repeatedly exposing the system to this vapor and then pumping the inlet system out. This was continued (4 h) until the D to H ratio in the mass spectrum of the mixture was constant. The neutral partial pressures of H_2O, HOD, and D_2O calculated from the L_2O^+ peak intensities agreed within 5% of those calculated from liquid vapor equilibrium data. At a partial pressure of L_2O of 1×10^{-6} torr at 25 °C in an ICR cell, with the instrument operating in the trapped ion mode,[13] all primary L_2O^+ ions produced at 70 eV rapidly lead to production of L_3O^+, eq 2. This

$$L_2O^+ + L_2O \rightarrow L_3O^+ + LO \qquad (2)$$

is followed by fast proton-deuteron exchange between L_3O^+ and L_2O to yield an equilibrium distribution of L_3O^+ ions. The distributions obtained from two different mixtures of $H_2O(l)$ and $D_2O(l)$, made up and run 10 months apart, are given in Table I.

At least 12 equilibrium constants involving single hydrogen ion transfers can be calculated from the values of ion and neutral concentration in Table I. All except three of these contain redundant information. Three reactions, eq 3-5, are chosen as

$$H_3O^+(g) + {}^1/_2D_2O(g) \rightleftharpoons {}^1/_2H_2O(g) + DH_2O^+(g) \qquad (3)$$

$$DH_2O^+(g) + {}^1/_2D_2O(g) \rightleftharpoons {}^1/_2H_2O(g) + D_2HO^+(g) \qquad (4)$$

$$D_2HO^+(g) + {}^1/_2D_2O(g) \rightleftharpoons {}^1/_2H_2O(g) + D_3O^+(g) \qquad (5)$$

representative. Equilibrium constants obtained are $K_3 = 2.07 \pm 0.25$, $K_4 = 0.85 \pm 0.05$, and $K_5 = 0.35\text{-}0.04$. The predominate factors in determining these equilibrium constants are the statistical factors of 3, 1, and ${}^1/_3$, respectively.[14]

The common reference for isotope effects is *liquid* water. Fractionation factors for the sequential replacement of H with D on the hydronium ion can be calculated by multiplying the equilibrium constants for reactions 3-5 by the fractionation factor for gaseous water of 0.93, eq 6, and dividing by the statistical

$${}^1/_2H_2O(g) + {}^1/_2D_2O(l) \rightleftharpoons {}^1/_2D_2O(g) + {}^1/_2H_2O(l) \qquad (6)$$

factors. Values obtained are $\phi_3 = 0.64 \pm 0.08$, $\phi_4 = 0.79 \pm 0.05$, and $\phi_5 = 0.97 \pm 0.11$. The variation of ϕ with successive deuteration indicates that D_2HO^+ and DH_2O^+ are less stable than would be expected on the basis of D_3O^+, H_3O^+ stabilities and the rule of the geometric mean.[15] These results indicate that replacement of hydrogen by deuterium in lyonium ions is an endothermic process, a consequence of the difference in zero point energies of the lyonium ions and isotopic water molecules.

The above data can be used to calculate a fractionation factor for the gaseous hydronium ion, ϕ_7, eq 7, of 0.79. This is larger

$${}^1/_3H_3O^+(g) + {}^1/_2D_2O(l) \rightleftharpoons {}^1/_3D_3O^+(g) + {}^1/_2H_2O(l) \qquad (7)$$

$$\phi_7 = 0.93(K_3K_4K_5)$$

than the value for the hydrated hydronium ion of 0.69 indicating that the force field of the gaseous hydronium ion is reduced less than that of the hydrated hydronium ion relative to liquid water. This is consistent with the recent spectroscopic observations of vibrational frequencies of gaseous H_3O^+ by Saykally[16] and Oka.[17] For example, the stretching frequencies ν_1 and ν_3 in H_3O^+ are determined to be 3520 and 3630 cm^{-1}, respectively, while those of H_2O are 3657 and 3756 cm^{-1}. It is of interest to note that the stretching frequencies in H_3O^+ are lower than those in H_2O even though the calculated O-H bond dissociation energies in H_3O^+ are larger indicating the importance of spectroscopic data in interpretation of isotope effects for gaseous ions.

The fact that the fractionation factor observed for gaseous H_3O^+ is identical with that in CH_3CN[10] is of considerable interest since it infers that hydrogen bonding from hydronium ion to acetonitrile has a negligible effect on the fractionation factor. Thus it appears that H_3O^+-CH_3CN interactions in acetonitrile solution are sufficiently weak to cause only minor changes in the force fields of H_3O^+ relative to those in the gas phase.

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Phosphorus-Sulfur Bond Order in Phosphorothioate Anions

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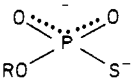
The question of negative charge localization between phosphorus-bonded oxygen and sulfur in aqueous solutions of phosphorothioate anions has long attracted attention in organophosphorus chemistry.[1] Owing to the absence of relevant physical data, uncertainties have often found expression in the use of chrage-delocalized structures. When negative charge was indicated as localized it was placed on oxygen, with sulfur being shown as doubly bonded to phosphorus.[2]

A recent review of available physical data indicates, however, that the structures of *O*-alkyl and *O*,*O*-dialkyl phosphorothioate anions in aqueous solutions should be represented as **1** and **2**, with



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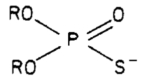

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