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(11) (η^5-C$_5$H$_5$)Mo(CO)$_3$H was prepared according to the literature procedure:[8]

$$\mathrm{Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2} \xrightarrow{\mathrm{Na/Hg}} 2[\mathrm{Mo(CO)_3(\eta^5\text{-}C_5H_5)}]^-$$

$$\xrightarrow{\mathrm{H^+}} 2[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Mo(CO)_3(H)}]$$

(12) The Mo(CO)$_2$(η^5-C$_5$H$_5$)(η^3-C$_5$H$_7$) isolated from the photoreaction was characterized by IR, ^{1}H NMR, and mass spectroscopy.

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Monte Carlo Computer Simulation of Hydrophobic Bonding

Sir:

The tendency of nonpolar solutes to associate spontaneously in aqueous solution at ordinary laboratory and physiological temperatures is presently recognized as one of the primary organizing principles of structural biochemistry and biology. A theoretical account of this phenomena, the hydrophobic interaction, was advanced by Kauzmann[1] some years ago and is now widely accepted.[2] However, it is clear from diverse recent contributions to the problem[3-5] that some detailed theoretical aspects of the process remain controversial. We report herein the first fully ab initio theoretical calculation of the hydrophobic interaction of nonpolar molecular solutes in liquid water, and comment on one currently debated point, the behavior of the solvent averaged interaction between hydrocarbon moieties as a function of separation. The prototype molecular system for the theoretical study of hydrophobic bonding is the dilute aqueous solution of two methane molecules, $[(CH_4)_2]_{aq}$.

In a series of recent contributions to this journal,[6-8] we reported statistical thermodynamic Monte Carlo computer simulation studies of the structure of liquid water and the dilute aqueous solution of methane, $[CH_4]_{aq}$, at 25 °C. The calculations were based on pairwise additive analytical potential functions representative of quantum mechanical calculations of intermolecular interactions.[9,10] The calculated structure of liquid water corresponded most closely to the energetic continuum model, and produced an average water coordination number of 4.2.[6] For $[CH_4]_{aq}$, clathrate-like contributions to the local solution environment of methane were directly identified, and the average methane coordination number was calculated to be 19.35.[7] The solvent in the vicinity of the solute was found to be ordered and energetically stabilized with respect to bulk water, independently confirming the prevalent conceptual model of hydrophobic hydration. For later reference, the aqueous phase effective radii for water and methane are R_{H_2O} = 1.38 and R_{CH_4} = 2.2 Å, estimated from the position of the first minima in our calculated radial distribution functions.[6,7]

We have recently extended our studies of water structure and hydrophobic hydration to problems in hydrophobic bonding. In computer simulation, the essential features of the hydrophobic interaction can be described in terms of a solvent averaged mean force $\langle F_z(R)\rangle$ between solute molecules as a function of the intersolute center-of-mass separation, R, and by the corresponding potential of mean force, $W(R)$. Recently, Pratt and Chandler[4] studied the interaction of spherical apolar species in a model water based on an integral equation method and predict an oscillatory behavior in $\langle F_z(R)\rangle$, implicating this result in a novel proposal for the folding of hydrocarbon chains. This contravened early Monte Carlo work on the problem by Dashevsky and Sarkisov[11] and the recent theoretical study by Clark et al.[5] based on the hypernetted chain approach. Pangali et al.[12] note a similar behavior for $\langle F_z(R)\rangle$ in molecular dynamics on Xe$_2$ in ST2 water. The calculations on $[(CH_4)_2]_{aq}$ reported herein introduce independent molecular level information on this problem and, by reference to our corresponding work on $[H_2O]_l$ and $[CH_4]_{aq}$, provide a structural interpretation of the $\langle F_z(R)\rangle$ results.

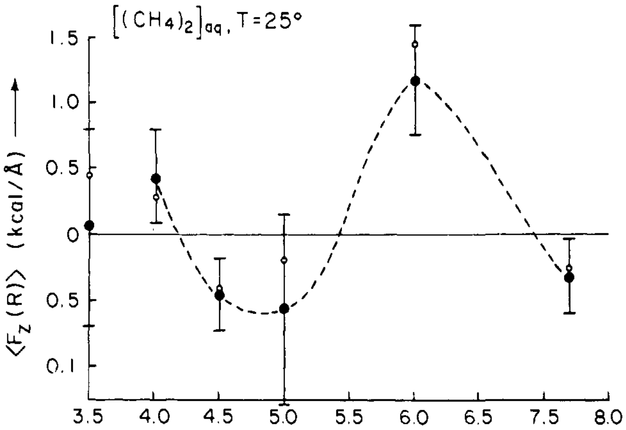

Figure 1. Calculated $\langle F_z(R)\rangle$ vs. R for $[(CH_4)_2]_{aq}$. The dots represent values computed by the direct procedure of ref 14. The circles represent values determined in an independent check based on finite differences. The error bars were established for each solid point from the corresponding maximum $[F_x(R), F_y(R)]$.

Our computer simulation on $[(CH_4)_2]_{aq}$ involved a system of two methane molecules and 214 water molecules at a temperature of 25 °C and a density calculated from the observed[13] partial molar volumes of methane (37 cm^3/mol) and water (18.06 cm^3/mol). The water-water and methane-water intermolecular potential functions and other characteristics of the calculations on $[(CH_4)_2]_{aq}$ were chosen to correspond as closely as possible to previous calculation on $[CH_4]_{aq}$, and the formalism and further detail is available in ref 8. The principle additional quantities computed here are the solvent-averaged forces $\langle F_i(R)\rangle$ ($i = x, y, z$) experienced by the center-of-mass of solute methane, determined here by the procedure suggested by McDonald and Rasaiah.[13] In an exact calculation, $\langle F_x(R)\rangle$ and $\langle F_y(R)\rangle$ would be expected to be zero, while $\langle F_z(R)\rangle$, the force along the intersolute coordinate, may be nonvanishing, and will be zero at the maxima and minima points in $W(R)$. In numerical calculations the residual magnitudes of $\langle F_x(R)\rangle$ and $\langle F_y(R)\rangle$ can be used to estimate error bounds on the calculated $\langle F_z(R)\rangle$ (Figure 1). The solvent averaged force is expected to be the dominant contribution to total force between nonpolar species in aqueous solution, as in the model system in ref 14.

Separate calculations were carried out for six solute intermolecular separations between 3.5 and 7.20 Å. The force calculations are each based on 800K to 1000K Monte Carlo Metropolis configurations after equilibration of the system. Each calculation required ~12 h on the CUNY IBM 370/168

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computer. Convergence of the calculations was monitored using control functions as described previously,[6,7] and elsewhere.[15] The solvent averaged force on the solute is clearly oscillatory as a function of R. The force vanishes at $R \simeq 4.2$, 5.15, and 7.0 Å and these distances should correspond to the calculated extrema in the $W(R)$ for the system. The extremum at 4.2 Å falls at the geometry $\sim 2R_{CH_4}$ expected for contact hydrophobic bonding. The average coordination number of the $[(CH_4)_2]_{aq}$ complex at the contact hydrophobic bonding distance is 24.5.

We infer that a maximum in $W(R)$ develops at 5.15 Å, followed by a second minimum at ~7.0 Å. This latter minimum distance corresponds to $\sim R_{CH_4} + 2R_{H_2} + R_{CH_4}$, two methanes approximately separated by a water molecular diameter. The average solvent coordination number of the $[(CH_2)_2]_{aq}$ complex at the solvent-separated hydrophobic bonding distance is 29.6. Our calculations thus support the possibility of a solvent-separated as well as contact hydrophobic bond.

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Evidence for the Synthesis of a "Stable" σ-Bonded Xenon-Carbon Compound: Bis(trifluoromethyl)xenon

Sir:

A target of prime interest since the pioneering work of Bartlett in xenon chemistry[1] has been the synthesis of a compound in which carbon is σ bonded to xenon. Such a species is a definite possibility in view of the recent synthesis of $FXeN(SO_2F)_2$[2] and evidence from ion cyclotron resonance experiments which estimate the strength of a xenon-carbon bond to be in the range of 43 ± 8 kcal/mol for $Xe(CH_3)^+$.[3] The less stable species $FXeCF_3$ has also been proposed as a reaction intermediate.[4]

Previously in our laboratory we have developed a general synthesis for trifluoromethyl organometallic compounds employing reactions of plasma generated radicals with metal halides:[5]

$$C_2F_6 \rightarrow 2CF_3\cdot$$

$$nCF_3\cdot + MX_n \rightarrow M(CF_3)_n + {}^n/_2X_2$$

$$X = I, Br, Cl$$

Considering the fact that xenon-fluorine bond strengths in XeF_2 are on the order of 31 kcal/mol, i.e. weaker than many of the halogen-metal bonds which have been broken in previous syntheses, synthesis of a xenon-carbon compound in this manner was thought to be a reasonable possibility. Crucial factors for the success of such a synthesis are (1) that the electronic rearrangement lifetime of the radical FXe· be long with respect to the collision frequency with an excess of trifluoromethyl radicals and (2) that, once formed in the free-radical process, the molecular species $Xe(CF_3)_2$ be stable enough to withstand collision and condensation.

By this synthetic method we were able to obtain a volatile, waxy, white solid which has a half-life of ~30 min when contained in a Kel-F container at room temperature. It has a much longer half-life (~2 weeks) at liquid nitrogen temperatures and decomposition is catalyzed by oxygen, glass, and moisture. This new compound, believed to be $Xe(CF_3)_2$, sublimes under vacuum with a vapor pressure significantly greater than that of XeF_2 and has very different physical properties. Thermal decomposition in the solid state while contained in a Kel-F tube gives xenon difluoride and at least six (GLC evidence) fluorocarbon products, presumably by a difluorocarbene elimination mechanism:

$$Xe(CF_3)_2 \xrightarrow{20\ ^\circ C} XeF_2 + C_nF_m$$

The XeF_2 produced appears as a highly crystalline solid on the Kel-F tube in contrast to the original waxy solid and the fluorocarbon layer separates over a 30-min period. Decomposition in the gas phase produces xenon and fluorocarbons including C_2F_6.

The synthetic procedure is identical with that reported previously[5] except that the entire plasma system is constructed of Teflon and other vacuum components are stainless steel and Kel-F. Xenon difluoride is bled into the tail of the trifluoromethyl radical plasma and the product is collected along with XeF_2 and fluorocarbons in a stainless steel trap at −196 °C. After the reaction is terminated the trap is warmed to −80 °C to remove unreacted C_2F_6. The white, waxy material is then separated from XeF_2 which is retained in a −35 °C trap on a Kel-F vacuum line. The product of interest condenses in a −78 °C trap and fluorocarbons pass on into a −196 °C trap. Separation may be performed several times and no significant quantities of XeF_2 are found after the initial separation. About 10 mg of product is produced in a 4-h time period.

One of the most compelling pieces of evidence for this compound is elemental analyses on samples of 1.88 and 0.85 mg for fluorine done after transporting the material at −196 °C to Schwarzkopf's Laboratories which gave 42.53 and 43.58% fluorine on duplicate samples. (Calcd for $Xe(CF_3)_2$: 42.33.)

The catalytic effect of polar surfaces such as AgCl, KBr, and CsI salt windows, resulting in the decomposition of $Xe(CF_3)_2$, leads to difficulty in obtaining an IR spectrum of the compound. Even when a CsI window was cooled to 35 K before sample deposition, decomposition to fluorocarbon products occurred as shown in Figure 1. By first depositing a layer of Xe and then a layer of $Xe(CF_3)_2$ at 35 K, we were able to ob-

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