ejection from the porphyrin π system, partly with the aid of MO calculations on a ground state of metalloporphyrin complexes. The metal dependence of the first two bands may be interpreted in terms of the inductive effect of metal ion, except for Fe and Co complexes. Then, the first (and the second) IP correlates well with the oxidation potential of porphyrin ring.

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Registry No. H_2OEP, 2683-82-1; MgOEP, 20910-35-4; FeOEP, 61085-06-1; CoOEP, 17632-19-8; NiOEP, 24803-99-4; CuOEP, 14409-63-3; ZnOEP, 17632-18-7; PdOEP, 24804-00-0.

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Properties and Reactions of Uranium(IV) Tetrahydroborate by Ion Cyclotron Mass Spectrometry

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The gas-phase ion chemistry of $U(BH_4)_4$ is studied with the techniques of ion cyclotron resonance spectrometry. An electron impact ionization energy of 9.0 ± 0.5 eV is determined, and appearance energies for several positive fragment ions are reported. These data are analyzed to give $\Delta H_f[U(BH_4)_4] = -7 \pm 14$ kcal/mol as well as several bond dissociation energies for the parent neutral and its fragment ions. $U(BH_4)_4$ attaches thermal electrons to form the molecular anion. Fragment negative ions are observed with higher energy electrons. The reactions of both positive and negative ions in $U(BH_4)_4$ alone and with other gases are reported. The trapped-electron spectrum is obtained and compared with previous optical spectroscopic studies of $U(BH_4)_4$. Irradiation of major positive ions by a low-power CW CO_2 laser produced no evidence of photochemistry.

Introduction

Uranium(IV) tetrahydroborate, $U(BH_4)_4$, is among the most volatile uranium compounds known.[1] To our knowledge, only the monomethyl derivative, $U(BH_4)_3(BH_3CH_3)$, and UF_6 have higher vapor pressures. Because of this, $U(BH_4)_4$ has been suggested as a unique source of atomic uranium.[2] In addition, the use of this species as a reagent in isotope separation has been proposed.[3]

Uranium(IV) hydroborate is of intrinsic interest because of the unusual nature of the bonding involved. In the gas phase, the molecular symmetry is tetrahedral. Each boron is attached to the uranium atom by three hydrogen bridges.[4] In crystalline form, six BH_4^- groups surround each uranium atom. Two of these retain the three-point attachment seen in the gas phase. The other four, using two-point attachment to each uranium, bridge neighboring uranium atoms in a helical polymeric structure.[5] The end result is an overall coordination number of 14, compared to 12 in the gas phase. In the similar zirconium(IV) tetrahydroborate, a tetrahedrally symmetric molecule, it has been shown by NMR that the hydrogens, both terminal and bridging, are indistinguishable.[6]

In the present investigation, we have undertaken to characterize the properties and reactions of $U(BH_4)_4$ and its ions both because there is potential technological importance of

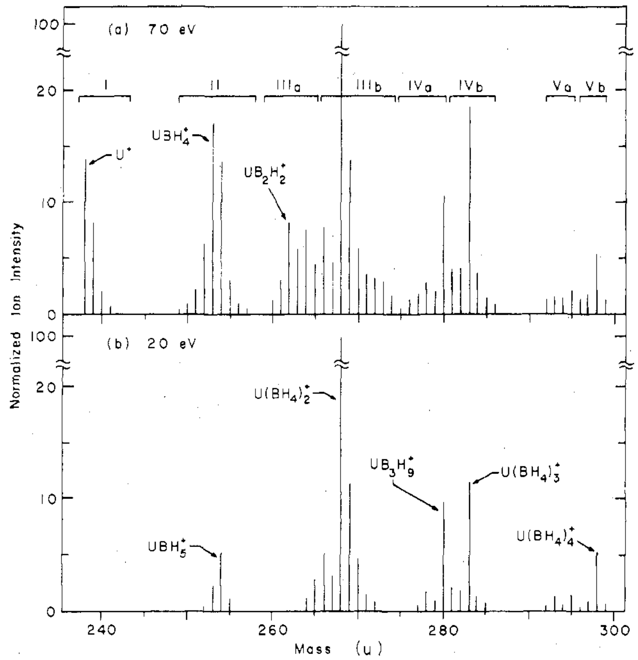

Figure 1. Monoisotopic ^{11}B positive ion mass spectra of $U(BH_4)_4$ at electron energies of (a) 70 eV and (b) 20 eV. The peaks are arbitrarily normalized to mass 268; intensity = 100. Major species are identified. The division into groups is explained in the text.

such information and because no mass spectral studies have yet been performed on either the uranium, zirconium, or analogous hafnium tetrahydroborates. Using the techniques of ion cyclotron resonance mass spectrometry, we have studied the ionization and fragmentation of the $U(BH_4)_4$ molecule. Both the positive and negative ion chemistry of uranium(IV) tetrahydroborate by itself and with other gases is reported. The trapped-electron spectrum[7,8] is obtained and compared with published optical spectra.

Experimental Section

Our sample of uranium(IV) tetrahydroborate, contained in a sealed-glass ampule with a break-seal, was the gracious gift of Professor E. R. Bernstein. The ampule was fitted with a stopcock which mated with a stainless steel gas handling system. The vapor pressure at ambient temperatures of $U(BH_4)_4$, a green crystalline solid, is approximately 0.1 torr[1] and proved adequate for all studies. When the sample was first admitted to the spectrometer, large amounts of diborane were present. This is presumably due to partial decomposition of the $U(BH_4)_4$ to uranium(III) tetrahydroborate, a nonvolatile solid.[1] The diborane was removed by briefly pumping directly on the sample. This procedure was repeated periodically throughout the investigation. Otherwise, the sample was used without further purification. All other chemicals were readily available from commercial sources and were used as supplied except for removal of noncondensable impurities at liquid nitrogen temperatures.

The ICR spectrometer used in these studies utilizes a 15-in. magnet system and was built in the machine shops of California Institute of Technology. This instrument and the techniques of ion cyclotron resonance spectrometry have been described in detail elsewhere.[9-12] Pressures were measured with a Schulz–Phelp-type ionization gauge calibrated at higher pressures for each component against a Baratron Model 90H1 capacitance manometer. All studies were performed at ambient temperatures (22 °C).

Resolution of the ICR in the drift mode was such that single masses could be resolved for species containing only one uranium atom. These spectra, Figures 1 and 3, have been corrected for the isotopes of boron (^{11}B, 80.6%). This deconvolution may be the cause of considerable error in the intensities given for species near major ions. When ions above 300 u were observed, resolution was sufficient only to discern varying numbers of borons. When this is the case, formulas of the form $U_lB_mH_n$ are used where n will be approximately 4 times m. When a specific species is indicated but not identified with certainty, a subscript in parentheses is given. In all cases, neutral species represented in reactions are merely inferred.

Table I. Appearance Energies and Calculated Heats of Formation for Fragment Ions of $U(BH_4)_4$

species	A, eV[a]	neutral products[b]	$\Delta H_f{}^\circ{}_{298}$, kcal/mol
U^+	12.8	$2B_2H_6 + 2H_2$	
UH^+	13.6	$2B_2H_6 + H_2 + H$	235
$UBH_4{}^+$	15.1	$B_2H_6 + BH_3 + H_2 + H$	254
$UBH_5{}^+$	13.5	$B_2H_6 + BH_3 + H_2$	269
group 3A	12.9[d]		
$U(BH_4)_2{}^+$	11.5	$B_2H_6 + H_2$	248
$UB_2H_9{}^+$	12.4	$B_2H_6 + H$	217
$UB_3H_9{}^+$	11.5	$BH_3 + 2H_2$	233
$UB_3H_{11}{}^+$	12.0	$BH_3 + H_2$	244
$U(BH_4)_3{}^+$	12.8	$BH_3 + H$	211
group 5A	11.7[d]		
$U(BH_4)_4{}^+$	9.0		201
$U(BH_4)_4$			−7 ± 14[c]

[a] Values given have an estimated error of ±0.5 eV. [b] The thermodynamically most stable neutral produts for a given fragmentation are assumed. $D(H-BH_3)$ is taken as 0. Other thermodynamic information used is given in Table II. [c] This value was calculated with the appearance energy of U^+. [d] These values were obtained under low-resolution conditions to enhance intensity.

Table II. Thermochemical Data

species	$\Delta H_f{}^\circ{}_{298}$, kcal/mol	ref
H	52.103 ± 0.001	*a*
BH_3	25.5 ± 10	*a*
B_2H_6	9.8 ± 4.0	*a*
U	125 ± 5	*b*
U^+	268 ± 5	*c*

[a] Reference 23. [b] S. D. Gabelnick, "Ion Reactor Safety and Physical Property Studies", Annual Report ANL-8120, Chemical Engineering Division, Argonne National Laboratory, July 1973–June 1974. [c] Calculated from $\Delta H_f(U)$ given above and IP(U) = 6.187 ± 0.002 eV given by G. S. Jones, I. Itzen, C. T. Pike, R. H. Levy, and L. Levin, *J. Quant. Electron.*, **QE-12**, 111 (1976).

Results

A. Positive Ion Mass Spectrometry. The 20- and 70-eV positive ion mass spectrum of $U(BH_4)_4$, reduced to monoisotopic ^{11}B form, is shown in Figure 1. The major peaks at 238, 253, 268, 283, and 298 u are assigned to the ions U^+, $UBH_4{}^+$, $U(BH_4)_2{}^+$, $U(BH_4)_3{}^+$, and the molecular ion $U(BH_4)_4{}^+$, respectively. Surrounding peaks are attributed to species having varying numbers of hydrogens. There is some uncertainty, however, in the assignment of peaks at 271–274 u. On the basis of the fact that ions at 274 and 275 u are the first to disappear as the electron energy is lowered, we take these two peaks as the dividing line between species containing two and three boron atoms. However, it seems clear that the ions $UB_3H_{0-3}{}^+$ also contribute to the peaks at 271–274 u.

Peaks of small intensity in the region where doubly ionized species would be expected were observed in the 70-eV spectrum. These ions were not further characterized. Peaks corresponding to masses 22–27 u were also observed. Their intensities agreed well with published mass spectra of diborane. It is therefore presumed that they are not fragment ions of $U(BH_4)_4$.

The spectrum is divided into eight groups, as shown in Figure 1, on the basis of the similar behavior of ions comprising a group as the electron energy is varied. This relative variation is depicted in Figure 2. Within these groups, the changes of individual species can be inferred by comparing the 20- and 70-eV spectra, with the exception of group 1. Here, the atomic ion U^+ is the major species at all energies examined. At 30 eV, however, the intensities of U^+, UH^+, and $UH_2{}^+$ are 1.0, 1.0, and 0.6, respectively. Appearance energies, listed in Table I, were obtained relative to Kr (IP = 13.999 eV)[13] by use of

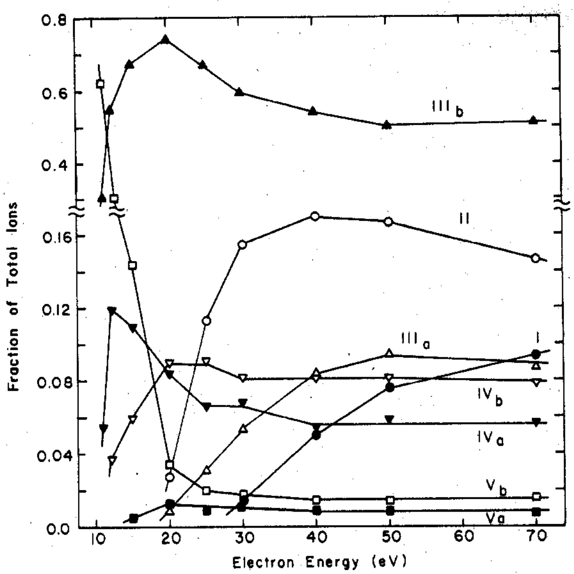

Figure 2. Breakdown diagram for $U(BH_4)_4$. The designations refer to the groups identified in Figure 1.

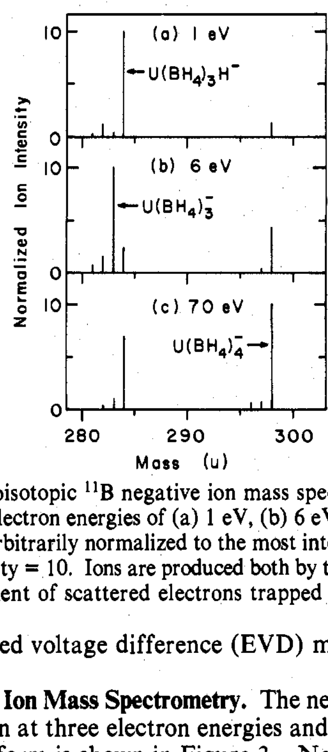

Figure 3. Monoisotopic ^{11}B negative ion mass spectra of $U(BH_4)_4$ at uncorrected electron energies of (a) 1 eV, (b) 6 eV, and (c) 70 eV. The peaks are arbitrarily normalized to the most intense ion for each spectrum; intensity = 10. Ions are produced both by the electron beam and by attachment of scattered electrons trapped in the ICR cell.

the extrapolated voltage difference (EVD) method of Warren.[14]

B. Negative Ion Mass Spectrometry. The negative ion mass spectrum taken at three electron energies and reduced to ^{11}B monoisotopic form is shown in Figure 3. No low-mass ions (such as BH_4^-) were observed nor were any species containing fewer than three borons. The major ions observed are formed by reactions 1–3. The branching ratio is strongly dependent

$$U(BH_4)_4 + e^- \rightarrow U(BH_4)_4^- \quad (1)$$

$$\rightarrow U(BH_4)_3H^- + BH_3 \quad (2)$$

$$\rightarrow U(BH_4)_3^- + BH_3 + H \quad (3)$$

on the energy of the impacting electron, as can be seen in Figure 3. Formation of the molecular anion occurs by attachment of thermal electrons. Processes 2 and 3 peak at energies of 0.4 ± 0.3 and 5.2 ± 0.3 eV, respectively. The electron energy scale was calibrated as outlined below for the trapped electron spectrum.

C. Positive Ion Chemistry. The temporal variation of ion concentration following a 10-ms, 20-eV electron beam pulse at a pressure of 1.5×10^{-6} torr is shown in Figure 4.

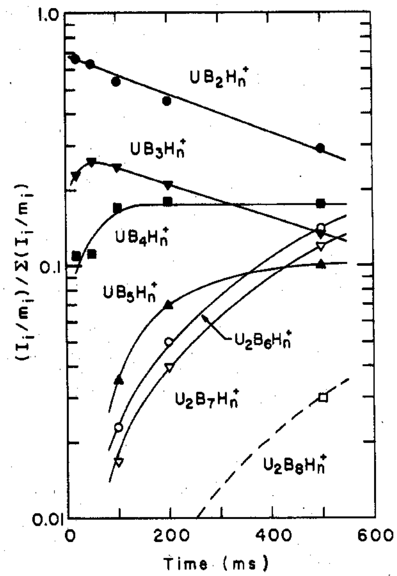

Figure 4. Temporal variation of positive ion abundances following a 10-ms, 20-eV electron beam pulse in 1.5×10^{-6} torr of $U(BH_4)_4$. Low-mass ions are not included.

Low-mass ions are not included. Double resonance identifies reactions 4 and 5 of the major low-mass ion $B_2H_5^+$, which

$$B_2H_5^+ + U(BH_4)_4 \rightarrow UB_3H_{(12)}^+ + B_2H_6 + BH_3 \quad (4)$$

$$\rightarrow UB_4H_{(15)}^+ + B_2H_6 \quad (5)$$

account for the increase in the species $UB_3H_n^+$ and $UB_4H_n^+$ at short times. Formation of $UB_5H_n^+$ takes place by the ligand-transfer process (6) which has a rate constant of 9×10^{-11} cm^3 molecule^{-1} s^{-1}.

$$UB_4H_{(16)}^+ + U(BH_4)_4 \rightarrow UB_5H_{(20)}^+ + U(BH_4)_3 \quad (6)$$

At long times, the positive ion chemistry is dominated by the formation of the dimeric species $U_2B_mH_n^+$. These ions appear to be products of cluster reactions:

$$UB_{(m-4)}H_{(n-16)}^+ + U(BH_4)_4 \rightarrow U_2B_mH_n^+ \quad (7)$$

The analogous processes

$$UF_n^+ + UF_6 \rightarrow U_2F_{n+6}^+ \quad (8)$$

where n = 3, 4, and 5, have been observed previously under similar conditions in our laboratories.[12] Rate constants for the cluster reactions, determined from the limiting slopes for disappearance of the reactant ions, are 3×10^{-11} cm^3 molecule^{-1} s^{-1}. This is in close agreement with the clustering rate constants obtained in the uranium hexafluoride study.[12] The upper mass limit in our experiments of approximately 740 u did not permit observation of product ions containing three or more uranium atoms. However, the trapped-ion data suggest that the dimeric uranium species react further but at a much slower rate, $k < 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Additional dimeric uranium species were also observed at higher pressures in drift-mode spectra. At a pressure of 1.2×10^{-5} torr and an electron energy of 20 eV, only $U_2B_6H_n^+$ and $U_2B_7H_n^+$ were observed. As the electron energy was raised, $U_2B_5H_n^+$ and $U_2B_4H_n^+$ were observed in conjunction with the appearance of UBH_n^+ and UH_n^+, thus identifying reactions 9 and 10.

$$UBH_n^+ + U(BH_4)_4 \rightarrow U_2B_5H_{n+16}^+ \quad (9)$$

$$UH_n^+ + U(BH_4)_4 \rightarrow U_2B_4H_{n+16}^+ \quad (10)$$

D. Negative Ion Chemistry The variation of negative ion abundances with time following a 10-ms, 70-eV electron beam

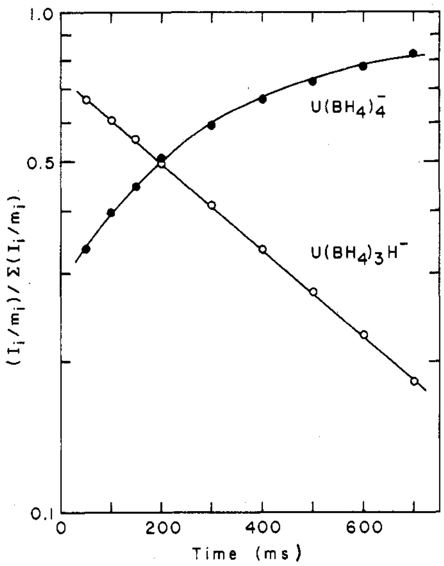

Figure 5. Temporal variation of anion abundances following a 10-ms, 70-eV electron beam pulse in 2.1×10^{-6} torr of $U(BH_4)_4$.

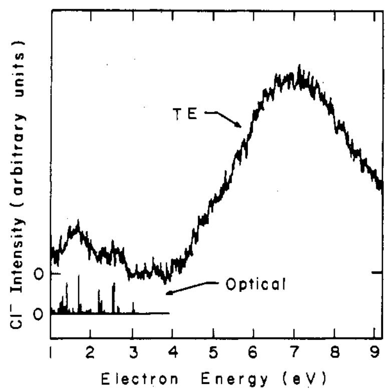

Figure 6. Trapped-electron (TE) spectrum of $U(BH_4)_4$ and a representation of the low-temperature (2 K) optical spectrum reported in ref 24. Zero intensity for the two spectra is offset for clarity.

pulse is shown in Figure 5. The rate constant for the reaction observed (eq 11) is 2.9×10^{-11} cm^3 molecule^{-1} s^{-1}. At 6 eV,

$$U(BH_4)_3H^- + U(BH_4)_4 \rightarrow U(BH_4)_4^- + U(BH_4)_3H \quad (11)$$

the similar process (eq 12) occurs with approximately the same

$$U(BH_4)_3^- + U(BH_4)_4 \rightarrow U(BH_4)_4^- + U(BH_4)_3 \quad (12)$$

rate constant. At higher pressures in the drift mode, a single dimer ion was detected. This species was the product of the clustering reaction

$$U(BH_4)_3H^- + U(BH_4)_4 \rightarrow U_2B_7H_{(29)}^- \quad (13)$$

E. Trapped-Electron Spectra. The threshold excitation spectrum of $U(BH_4)_4$, obtained by monitoring Cl^- ions produced by the dissociative attachment process of eq 14, is shown

$$CCl_4 + e^- \text{ (0 eV)} \rightarrow CCl_3 + Cl^- \quad (14)$$

in Figure 6. The basic experimental method has been previously described.[7,8] The incident electron current was 2×10^{-6} A, and the trapping voltage was −0.2 V. Partial pressures of $U(BH_4)_4$ and CCl_4 were about 10^{-4} and 10^{-6} torr, respectively. The energy scale was calibrated by taking the B $^3\Pi_g$ excitation of nitrogen at 7.8 eV[15] as reference and assuming the energy scale correction to be independent of the electron acceleration voltage. The resolution is approximately 0.2 eV.

F. IR Laser Studies. An attempt was made to observe the IR laser photochemistry of the ions of $U(BH_4)_4$. The experimental methods used have been previously described.[16] No change in the intensities of $UB_2H_n^+$, $UB_3H_n^+$, and $UB_4H_n^+$ nor $U_2B_6H_n^+$ and $U_2B_7H_n^+$ were observed upon irradiation with a low-power CW CO_2 laser. Several wavelengths and ionizing energies were used.

Discussion

At high electron energies (greater than 30 eV), the dominant fragmentation process upon ionization of $U(BH_4)_4$ appears to be successive loss of BH_4 ligands. However, the BH_4 molecule is not expected to be stable. It has never been observed directly, although it has been postulated as a transient intermediate in the pyrolysis of diborane.[17] Calculations give the bond energy between a hydrogen atom and a BH_3 molecule as only 0.003 kcal/mol.[18] Thus, at lower electron energies, fragmentation routes involving thermodynamically stable neutral species predominate. For example, processes 15 and

$$U(BH_4)_4 + e^- \rightarrow UB_3H_9^+ + BH_3 + 2H_2 + 2e^- \quad (15)$$

$$\rightarrow UB_3H_{11}^+ + BH_3 + H_2 + 2e^- \quad (16)$$

$$\rightarrow U(BH_4)_3^+ + BH_3 + H + 2e^- \quad (17)$$

16 have an appearance threshold below that for reaction 17. Particularly indicative of this trend is the surprising intensity of $U(BH_4)_2^+$, by far the major ion at all electron energies above about 13 eV. By contrast, UF_2^+ formed in the 50-eV ionization of UF_4 is less than one-sixth as intense as UF_3^+, the major ion.[19] The predominance of $U(BH_4)_2^+$ strongly suggests that B_2H_6 and H_2 are the neutral species produced upon fragmentation and not two BH_4 groups. This trend is also implied in the production of U^+. Here, the appearance energy for U^+ is 0.8 eV less than that for UH^+, indicating a hydrogen molecule must be produced in the former fragmentation process.

On the assumption that in all cases the appearance energy of a fragment ion corresponds to production of the thermodynamically most favorable neutral species, the heats of formation listed in Table I can be calculated. The heat of formation for the neutral $U(BH_4)_4$ molecule is calculated to be -7 ± 14 kcal/mol from process 18. It is well recognized

$$U(BH_4)_4 + e^- \rightarrow U^+ + 2B_2H_6 + 2H_2 + 2e^- \quad (18)$$

that electron impact appearance energies for ions resulting from extensive fragmentation are often higher than the thermodynamic limit. Thus, this heat of formation may also be an upper limit. Using the heat of formation derived for UH^+, we can also calculate the bond dissociation energy, $D(U^+\text{–}H)$, as 3.7 ± 0.8 eV. This is in reasonable agreement with literature values of 2.9 ± 0.1[20] and 3.3 ± 0.5 eV,[21] lending credence to the assumptions involved in the computation.

Also of interest is the average binding energy of a BH_4 group to both the uranium atom and ion. For the former, $\bar{D}[U\text{–}(BH_4)_4]$ equals 4.8 ± 0.7 eV, and for the latter, $\bar{D}[U^+\text{–}(BH_4)_4]$ equals 4.1 ± 0.7 eV. Since the loss of a BH_4 group may be thought of as the breaking of four one-electron half-bonds (three U–H bonds and one B–H bond), the mean half-bond dissociation energy is 1.2 eV for the neutral complex and 1.0 eV for the ion. These figures can be compared favorably with the average half-bond dissociation energy in B_2H_6 of 0.9 ± 0.4 eV.[22] The energy necessary to effect the successive loss of BH_4 groups from $U(BH_4)_4^+$ occurs in the sequence 3.8, 5.0, 3.6, and 4.0 eV. Curiously, while the highly favorable process of eq 19 has a calculated heat of reaction of 2.5 eV, the

$$U(BH_4)_4^+ \rightarrow U(BH_4)_2^+ + B_2H_6 + H_2 \quad (19)$$

subsequent loss of B_2H_6 and H_2 to yield U^+ is even more favorable energetically, $\Delta H_r = 1.3$ eV. Since the intensity of the uranium ion never approaches that of $U(BH_4)_2^+$, the second process may involve a substantial rearrangement.

As with positive ions, the formation of anions primarily involves neutral fragments which are thermodynamically stable. Thus, loss of BH_3 from $U(BH_4)_4^-$ occurs at a lower energy than loss of BH_4. Since the molecular anion is formed by attachment of thermal electrons, $U(BH_4)_4$ must have a positive electron affinity (EA). An attempt was made to determine this value by observing electron-transfer reactions with anions whose electron affinities are known. No such reaction was observed with F^- (EA = 3.4 eV)[23] nor with NO_2^- (EA = 2.4 eV).[23] This behavior is in contrast to that of UF_6[12] which undergoes exothermic charge transfer with Cl^- (EA = 3.6 eV).[23] While the present result is inconclusive, an upper limit on the electron affinity of $U(BH_4)_4$ may be inferred (<2.4 eV).

In general, the major reactions observed for the positive and negative ions of $U(BH_4)_4$ lead to an increase in the coordination number of the uranium atom within the ion. This is true for the ligand-transfer reaction (6), which produces a U(VI) ion species, and for the electron-transfer reactions (11) and (12), which form the molecular anion, a U(III) species. The cluster reactions also conform to this pattern of reactivity.

Clustering of positive ions occurs much more readily than does that of the negative ions of $U(BH_4)_4$. In the study on UF_6,[12] this same result prompted the suggestion that the dimer species were "onium" ions, uranium atoms bridged by a positively charged fluorine. The analogous structure in the present case would contain a bridging BH_4^- group similar to those observed in $U(BH_4)_4$ crystals. The ionic character of $U-(BH_4)$ bonds inhibits formation of stable dimers with the electron-rich negative ions. Since the only negative dimer observed is $U_2(BH_4)_7H^-$, some type of hydride bridge may be implied.

On consideration of the resolution, the correspondence below 4 eV between the trapped-electron (TE) spectrum and the optical spectrum (taken at 2 K), shown in Figure 6, is quite good. Bernstein and Keiderling[24] assigned these peaks as electronic–vibronic excitations composed primarily of d–d transitions. They also reported that an intense charge transfer and/or f–d transition cutoff commences at 2900 Å (4.28 eV). This is in good agreement with the TE spectrum. Ghiasse, Clay, and Walton[25] observed a band at 4.9 eV in their gas-phase UV absorption spectrum. This feature compares well with the shoulder seen in the TE spectrum. While more obvious in other spectra, the shoulder could never be fully resolved. It is interesting to note that this shoulder matches the peak observed for formation of $U(BH_4)_3^-$ by electron impact on $U(BH_4)_4$, suggesting that this transition is indeed a ligand to metal charge-transfer band. Assignment of the intense feature at 7 eV is uncertain.

Conclusion

The use of uranium(IV) tetrahydroborate as a source of atomic uranium seems well justified. The heat of reaction for process 20 is only 6.6 eV, well below that for the analogous

$$U(BH_4)_4 \rightarrow U + 2B_2H_6 + 2H_2 \qquad (20)$$

decompositions of UF_6 (eq 21) and UF_4 (eq 22) at 27.6 and

$$UF_6 \rightarrow U + 3F_2 \qquad (21)$$

$$UF_4 \rightarrow U + 2F_2 \qquad (22)$$

21.8 eV,[26] respectively. It also seems likely that photolysis of $U(BH_4)_4$ at 250 nm, ~5 eV, would induce its decomposition to $U(BH_4)_3$.

While the structure of ions cannot be investigated directly, certain conclusions can be inferred. Namely, the smaller ions, such as $U(BH_4)_2^+$, probably do not retain the three-point attachment observed in gas-phase $U(BH_4)_4$. In addition, positive ions containing two uranium atoms are likely joined by the BH_4 bridging structure which is seen in crystalline $U(BH_4)_4$.

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