Thermochemistry of Uranium Halide Ions. Reactions of U<sup>+</sup> with CH<sub>3</sub>F, SiF<sub>4</sub>, CH<sub>3</sub>Cl, and 

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An ion beam apparatus was used to examine the reactions of U<sup>+</sup> with CH<sub>3</sub>F, SiF<sub>4</sub>, CH<sub>3</sub>Cl, and CCl<sub>4</sub>. Reaction with the methyl halides to yield  $UX^+$  is exothermic for both X = F and Cl. Reaction with the tetrahalides yields both  $UX^+$  and  $UX_2^+$ . With  $CCl_4$ , these processes are exothermic while with SiF<sub>4</sub>, they are endothermic. Interpretation of the threshold for UF<sup>+</sup> formation from SiF<sub>4</sub> allows the values  $D^{\circ}(U^+-F) = 113 \pm 12 \text{ kcal/mol}$ and  $\Delta H_{f}^{\circ}(UF^{+}) = 177 \pm 13$  kcal/mol to be derived. When an estimate of 6.7 ± 1 eV is used for the ionization potential of uranium monofluoride,  $\Delta H_{\rm f}^{\circ}({\rm UF}) = 22 \pm 27$  kcal/mol and  $D^{\circ}({\rm U-F}) = 125 \pm 27$  kcal/mol are also derived.

# Introduction

Despite the interest in such information, published thermodynamic data regarding uranium halides, especially the mono- and dihalides, are scarce. For the technologically important U-F system, the available data have been compiled by Gurvich et al.<sup>1</sup> and by Hildenbrand.<sup>2</sup> Neither report any experimental results for uranium monofluoride although Gurvich et al. estimate that  $\Delta H_{f}^{\circ}(\text{UF}) = -3 \pm$ 6 kcal/mol at 0 K and that the ionization potential of UF is  $6.7 \pm 1 \text{ eV}$  based on comparisons with WF. Appearance potential measurements on  $UF_6$  yield values for the heats of formation of UF<sup>+</sup> and UF<sub>2</sub><sup>+</sup> which are clearly too high.<sup>3,4</sup> Essentially no thermochemical data are available for the uranium chlorides.

In this paper, we investigate the formation of  $UF^+$ ,  $UF_2^+$ , UCl<sup>+</sup>, and UCl<sub>2</sub><sup>+</sup> in reactions of U<sup>+</sup> with various halogencontaining species. Use of an ion beam apparatus in these studies allows the first direct experimental determination of  $\Delta H_{f}^{\circ}(UF^{+})$  and provides limits on the heats of formation for  $UF_2^+$ ,  $UCl^+$ , and  $UCl_2^+$ . The present study is an extension of previous work concerning the reactivity of uranium ions with a wide variety of species.<sup>5,6</sup>

#### **Experimental Section**

The ion beam apparatus, experimental techniques, and U<sup>+</sup> source have been detailed previously.<sup>5-7</sup> Briefly, dissociation of  $UF_4$  and surface ionization of the resultant uranium atoms occur on a resistively heated rhenium filament. These ions are extracted, mass and energy selected, and focused into a collision number containing the reactant gas. Product ions are analyzed by a quadrupole mass filter and detected with a Channeltron electron multiplier. Ion intensities are corrected for the mass discrimination of the quadrupole. Gas samples were obtained from commercial sources and used as supplied except for removal of noncondensable impurities at liquid nitrogen temperatures.

Reaction cross sections are calculated by use of

$$\sigma_{\rm i} = \sigma I_{\rm i} / \Sigma I_{\rm i} \tag{1}$$

$$I_0 / (I_0 + \Sigma I_i) = e^{-n\sigma l}$$
<sup>(2)</sup>

where  $I_i$  and  $I_0$  are the product ion current and transmitted  $U^+$  ion current, respectively, n is the density of the target gas, and l is the length of the interaction region ( $\sim 5$  mm).

The largest error associated with measurement of these cross sections is the ion collection efficiency. This efficiency is presumed to be quite high in the present studies because the masses of the ionic reactant and products are large relative to the neutrals involved. In agreement with this is the observation that an extraction field placed across the collision chamber had little effect on product ion yields. We estimate the cross sections reported are accurate to within a factor of two.

### **Results and Discussion**

Reaction with Methyl Halides. Uranium ions react with methyl halides to produce the uranium monohalide ion, reaction 3, where the halogens examined are fluorine and

$$U^{+} + CH_{3}X (X = F, Cl) \rightarrow UX^{+} + CH_{3}$$
(3)

chlorine. At the lowest energies examined, the reaction cross sections decrease monotonically with increasing energy (Figures 1 and 2). This is typical of exothermic reactions and establishes that  $D^{\circ}(U^{+}-F) > D^{\circ}(CH_{3}-F) =$  $110 \pm 7 \text{ kcal/mol}^8$  and that  $D^{\circ}(U^+-Cl) > D^{\circ}(CH_3-Cl) =$  $84 \pm 1 \text{ kcal/mol.}^8$ 

In the methyl fluoride system (Figure 1), the reaction cross section shows a peak at approximately the methyl fluoride bond energy. While somewhat unusual, this overall behavior in the cross section has precedent.<sup>6,9</sup> The simultaneous operation of two reaction mechanisms, insertion and abstraction, may be responsible for this behavior. Insertion of U<sup>+</sup> into the methyl fluoride bond should be the lowest energy reaction pathway and is, presumably, exothermic. Direct abstraction of the F atom by U<sup>+</sup> is then postulated to account for the peak observed in the cross section. This process has a threshold energy

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**Figure 1.** Variations in cross section for reaction of U<sup>+</sup> with methyl fluoride as a function of kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale). The dashed line shows the cross section predicted by use of the LGS model (see text). The arrow marks the bond dissociation energy of  $CH_3F$ , 4.77 eV. The slopes of the straight line portions of the experimental cross section are also given.



**Figure 2.** Variation in cross section for reaction of U<sup>+</sup> with methyl chloride as a function of kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale). The dashed line shows the cross section predicted by using the LGS model (see text). The arrow marks the bond dissociation energy of CH<sub>3</sub>Cl, 3.64 eV. The slope of the straight line, an approximate fit to the data, is also given.

estimated to be several tenths of an electronvolt in the center of mass, even though the overall reaction is exothermic. While both mechanisms are probably operative in the methyl chloride system, there is not a pronounced peak in the cross section. The data in Figure 2 are more typical of exothermic reactions.

In the  $CH_3Cl$  system, the product  $UCl^+$  is observed at higher pressures of  $CH_3Cl$  to react further to form  $UCl_2^+$  (reaction 4). This process is also exothermic, indicating

$$UCl^{+} + CH_{3}Cl \rightarrow UCl_{2}^{+} + CH_{3}$$
(4)

that the second uranium ion chlorine bond is also greater than 84 kcal/mol. While the analogous reaction was not observed in the methyl fluoride system, a full range of pressures was not examined.



**Figure 3.** Variation in cross section for reaction of U<sup>+</sup> with carbon tetrachloride as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). The short dashed line gives the total cross section for both reaction channels. The long dashed line shows the cross section predicted by using the LGS model (see text). The arrow marks the bond dissoclation energy,  $D^{\circ}(CCl_3-CI) = 3.1 \text{ eV}$ . The slopes of the straight line portions of the experimental cross sections are also given.

Reaction with  $CCl_4$ . Uranium ions react with carbon tetrachloride to produce both UCl<sup>+</sup> and UCl<sub>2</sub><sup>+</sup>, reactions 5 and 6. It was verified that formation of UCl<sub>2</sub><sup>+</sup> was the

$$U^{+} + CCI_{4} - UCI^{+} + CCI_{3}$$
 (5)  
 $UcI_{2}^{+} + CCI_{2}$  (6)

result of a single bimolecular collision, i.e., reaction 6, by examining the pressure dependence of the cross section for this product.<sup>10</sup> The reaction cross sections shown in Figure 3 indicate both processes are exothermic with UCl<sup>+</sup> being the predominant product at all energies examined. The relative behavior of the UCl<sup>+</sup> and UCl<sub>2</sub><sup>+</sup> cross sections is understandable since formation of UCl<sub>2</sub><sup>+</sup> requires more rearrangement and thus involves a longer lived intermediate than UCl<sup>+</sup> formation. Increasing the U<sup>+</sup> kinetic

energy decreases the lifetime of the intermediate making  $UCl_2^+$  formation progressively less likely than production of  $UCl^+$ . The exothermicity of reaction 5 requires that  $D^{\circ}(U^+-Cl) > D^{\circ}(CCl_3-Cl) = 71 \pm 2 \text{ kcal/mol},^8$  in agreement with the  $CH_2Cl$  results. The exothermicity of reaction 6 implies

>  $D^{\circ}(CCl_3-Cl) = 71 \pm 2 \text{ kcal/mol},^{\circ}$  in agreement with the CH<sub>3</sub>Cl results. The exothermicity of reaction 6 implies that  $D^{\circ}(ClU^+-Cl) > 138 \pm 5 \text{ kcal/mol}^8 - D^{\circ}(U^+-Cl)$ .

Reaction with  $SiF_4$ . Reaction of uranium ions with silicon tetrafluoride yields both UF<sup>+</sup> (reaction 7) and UF<sub>2</sub><sup>+</sup> (reaction 8). It was verified that formation of UF<sub>2</sub><sup>+</sup> was

$$U^{\dagger} + SiF_4 - \bigcup F^{\dagger} + SiF_3 \qquad (7)$$

$$UF_2^{\dagger} + SiF_2 \qquad (8)$$

the result of only a single bimolecular collision, i.e., reaction 8, by examining the pressure dependence of the cross section for this product.<sup>10</sup> The experimental results, shown in Figure 4, indicate both reactions are endothermic. The signal observed at low energies is believed to result from reaction at higher energies outside the collision chamber.

While the endothermicity of reaction 5 gives an upper limit to the uranium ion-fluorine bond of  $D^{\circ}(SiF_3-F) =$ 



**Figure 4.** Variation in cross section for reaction of  $U^+$  with silicon tetrafluoride as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). The arrow indicates the threshold for reaction 7, 1.4 eV (see text). The solid line is the fit to the data described in the text.

 $145 \pm 3 \text{ kcal/mol}$ ,<sup>8</sup> a more specific value can be obtained by fitting the data for UF<sup>+</sup> with an energy dependent cross section. We choose the form of eq 9, where  $E_0$  is the

$$\sigma(E) = \sigma_0 [(E - E_0)/E]^n \tag{9}$$

threshold energy,  $\sigma_0$  is an energy independent cross section, and n is a variable parameter. This equation, considered in detail elsewhere,<sup>7</sup> has been shown to be useful in interpreting such data.<sup>6,7</sup> The fit shown in Figure 4 uses n= 2,  $\sigma_0$  = 9.4 Å<sup>2</sup>, and  $E_0$  = 1.4 eV. Reasonable fits are also obtained for n = 1-4 corresponding to thresholds of 1.9-0.9 eV. The threshold obtained suggests  $D^{\circ}(U^{+}-F) = 113 \pm$ 12 kcal/mol, which is in agreement with the results for the methyl fluoride system. This bond energy corresponds to a heat of formation of  $177 \pm 13$  kcal/mol for UF<sup>+,11</sup> a value consistent with the estimate made by Gurvich et al.<sup>1</sup> of 152  $\pm$  24 kcal/mol. Our value may also be compared with a lower limit of 168 kcal/mol<sup>10</sup> implied by the exothermicity of reaction 10 observed in ICR studies of  $UF_6$ ,<sup>12</sup> and with an upper limit of approximately 200 kcal/mol derived from the appearance potential of  $UF^+$  from  $UF_{6}$ .<sup>3</sup>

$$\mathrm{UF}^{+} + \mathrm{UF}_{6} \rightarrow \mathrm{UF}_{2} + \mathrm{UF}_{5}^{+} \tag{10}$$

Use of this experimental heat of formation and the estimate of Gurvich et al.<sup>1</sup> for the ionization potential of uranium monofluoride, IP(UF) =  $6.7 \pm 1$  eV, gives  $\Delta H_f^{\circ}(\text{UF}) = 22 \pm 27$  kcal/mol and  $D^{\circ}(\text{U-F}) = 125 \pm 27$ kcal/mol.<sup>11</sup> This estimate for the ionization potential is consistent with the observation that the amount of UF<sup>+</sup> produced by our surface ionization source is only about

TABLE I: Thermochemical Data for Uranium Species<sup>a</sup>

species (M)	$\Delta H_{\mathbf{f}}^{\circ}(\mathbf{M}),$ kcal/mol	IP(M), eV	$\Delta H_{\mathbf{f}}^{\circ}(\mathbf{M}^{+}),$ kcal/mol
U UF	$   \begin{array}{r} 128 \pm 2^{b} \\     22 \pm 27 \\     <34 \pm 13   \end{array} $	$\begin{array}{c} 6.19 \pm 0.06^{b} \\ 6.7 \pm 1^{b} \\ > 6.2^{c} \end{array}$	$271 \pm 2$ $177 \pm 13^{c}$
UF <sub>2</sub>	$-134 \pm 7^b$	$6.8 \pm 0.5^{b}$	$23 \pm 14 < 55 \pm 12^{c} < 19 \pm 6^{d}$
UCl UCl <sub>2</sub>			$<216 \pm 3^{c}$ $<191 \pm 6^{c}$

<sup>a</sup> All thermochemical data at 298 K. Values without reference are calculated from other data in this table. <sup>b</sup> Reference 4. <sup>c</sup> This work. <sup>d</sup> Reference 13.

1% of the U<sup>+</sup> formed.<sup>5</sup> This observation indicates that  $IP(UF) > IP(U) \simeq 6.2 \text{ eV}^{11}$  and, consequently, that  $\Delta H_f^{\circ}(UF) < 34 \pm 13 \text{ kcal/mol.}$ 

With an analysis similar to that described above, an apparent endothermicity for reaction 8 of  $1.3 \pm 0.5$  eV is derived. Because of the complexity of this reaction, no specific thermochemistry can be inferred from this result. However, this threshold does suggest an upper limit of  $55 \pm 12$  kcal/mol to the heat of formation of UF<sub>2</sub><sup>+</sup>. This is consistent with the value of  $23 \pm 14$  kcal/mol reported by Gurvich et al.<sup>1</sup> The associative ionization reaction 11, reported by Fite,<sup>13</sup> implies an upper limit of  $19 \pm 6$  kcal/mol for  $\Delta H_{\rm f}^{\circ}({\rm UF_2}^+)$ .

$$U + SF_6 \rightarrow UF_2^+ + SF_4 + e^- \tag{11}$$

## Conclusion

A compilation of the thermochemistry derived in this study is given in Table I. The upper limits found for  $\Delta H_f^{\circ}(\text{UCl}^+)$  and  $\Delta H_f^{\circ}(\text{UCl}_2^+)$  are probably quite high. The value for  $\Delta H_f^{\circ}(\text{UF})$  indicates the first uranium-fluorine bond is weaker than the second,  $125 \pm 27$  kcal/mol compared to  $175 \pm 28$  kcal/mol. This is in keeping with the relative values of the third and fourth uranium-fluorine bond energies,  $138 \pm 9$  and  $151 \pm 6$  kcal/mol,<sup>11</sup> respectively.

In Figures 1-3, the experimental results are compared with the Langevin-Gioumousis-Stevenson (LGS) model given by eq 12, where E is the relative collision energy, e

$$\sigma(E) = \pi e (2\alpha/E)_{1/2} \tag{12}$$

is the electron charge, and  $\alpha$  is the rotationally averaged polarizability of the neutral reactant.<sup>14</sup> As noted in a previous study of U<sup>+</sup> reactions, the LGS model, while yielding the correct magnitude for reaction cross sections, does not produce consistent quantitative agreement with the experimental results.

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<sup>(11)</sup> Calculated by using the thermodynamic information concerning uranium containing species taken from ref 1 and auxiliary thermochemistry as in ref 8.

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