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Ion-molecule reactions of SF₆: Determination of I.P.(SF₅), A.P.(SF₅⁺/SF₆), and $D(SF_5-F)^{a}$

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SF₆ reacts with CF₃⁺ to produce SF₅⁺ and CF₄. Under conditions of large amounts of CF₄, an equilibrium is established. From flowing afterglow data, not only is a forward rate constant $k_f = (2.5 \pm 0.2) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ determined, but also an equilibrium constant of 5.9×10^3 ($\pm 50\%$) is deduced. Using this equilibrium constant and standard entropies for the various species, $\Delta H_{298}^{\circ} = -0.17 \pm 0.02$ eV is calculated. A thermochemical cycle then yields a value of A.P.(SF₅⁺/SF₆) = 14.62 ± 0.09 eV. An examination of charge exchange reactions of SF₅⁺ leads to establishment of the ionization potential of SF₅ at 10.5 ± 0.1 eV. Combining this with A.P.(SF₅⁺/SF₆) allows a calculation of the bond dissociation energy $D_{298}^{\circ}(SF_5-F) = 4.1 \pm 0.13$ eV. In addition to these new values of A.P.(SF₅⁺/SF₆), I.P.(SF₅), and $D_{298}^{\circ}(SF_5-F)$, the fragmentation pattern of SF₆ reacting with He⁺ as well as rates of reaction of SF₆ with several positive ions are reported.

I. INTRODUCTION

Since the first separation in 1975 of sulfur isotopes by laser irradiation, 1 SF₆ has been a molecule of considerable interest. It has been investigated as a source of F atoms in lasers, and its properties as an electron scavenger have been widely studied. ${}^{2-6}$ Recently, the IR multiphoton dissociation of SF₆ has received much attention, both experimentally^{7,8} and theoretically. 9 Because SF₆ has been used as a model compound for the study of laser induced chemistry and for the study of laser isotope separation, an accurate knowledge of its thermodynamic parameters is of tremendous importance.

The early work of Kay and Page¹⁰ placed the SF₅-F bond energy at 3.73 ± 0.13 eV. However, several other measurements 11(a)-(c) of this bond dissociation energy placed it at 3.3-3.4 eV, and this lower number became the critically accepted value for $D_0^{\circ}(SF_5-F)$. More recently, studies have been made which indicate that the SF5-F bond energy is larger than any of these previously reported values. Lyman¹² has used RRKM unimolecular reaction rate theory to calculate a bond dissociation energy of 3.99 eV, and Benson¹³ has arrived at a value of 4.03 ± 0.13 eV on the basis of a reanalysis of the shock tube data of Bott and Jacobs.^{11(b)} In a study of the chemiluminescence of reactions of SF_6 with metastable calcium and strontium, Kiang and Zare¹⁴ have been able to place limits on $D(SF_5-F)$, and they conclude that $D_0^\circ = 3.95 \pm 0.14$ eV.

The appearance potential of SF_5^+ from neutral SF_6 has been measured using a number of different techniques. All of these previously obtained values are above 15 eV: 15.29 eV determined by photoionization, ¹⁵ 15.35 eV determined by photoelectron spectroscopy, ¹⁶ and 15.50 eV determined by electron impact mass spectrometry. ^{11(c)}

In the work reported here, the flowing afterglow technique was used to study the ion-molecule reactions of SF_6 . Thermochemical information may be obtained from two types of flowing afterglow measurement. The first is a "yes/no" method. By studying the charge exchange reactions of a neutral B with an ion A⁺, one can place

^{a)}Work performed under the auspices of the U. S. Department of Energy.

limits upon the ionization potential of A if the ionization potential of B is known. That is, if the reaction $A^* + B^* \rightarrow B^* + A$ occurs, then one can conclude that I.P. $(A) \ge I.P.(B)$. Conversely, if the reaction does not occur, then I.P.(A) < I.P.(B). In charge exchange processes involving polyatomic ions. it is possible that the presence or absence of reaction may be influenced by internal energy, symmetry rules, or reaction barriers, so it is important, if possible. to test such reactions in both directions. If the charge exchange proceeds in at least one direction and the presence of reactant internal energy can be ruled out, then the conclusions reached above are confirmed. The second method for obtaining thermodynamic parameters from flowing afterglow experiments is through the study of equilibrium systems. Here equilibrium constants, and thus free energies of reaction, can be calculated. From these, thermochemical cycles can be constructed from which thermodynamic values such as bond energies and appearance potentials can be obtained.

We have examined the equilibrium system $CF_3^* + SF_6$ $\Rightarrow SF_5^* + CF_4$, and are able to calculate an appearance potential of SF_5^* from SF_6 . An independent measurement of the $Kr^* + SF_6$ charge exchange reaction corroborates this new value. In addition, some charge exchange reactions of the SF_5^* ion have been examined, and a value of I. P. (SF_5) is reported. Combination of A. P. (SF_5^*/SF_6) with I. P. (SF_5) then permits calculation of the SF_5-F bond strength. Each of these thermochemical studies will be discussed, and the new values for A. P. (SF_5^*/SF_6) , I. P. (SF_5) , and $D(SF_5-F)$ obtained will be presented.

Finally, we have also investigated the reactions of SF_6 with some small positive ions. In addition to corroborating some rate constants of early work of Fehsenfeld, ¹⁷ we have extended the investigation of the ion-molecule reactions of SF_6 to include the reactions of several new ions. We also report the fragmentation pattern produced by the reaction of SF_6 with helium ions.

II. EXPERIMENTAL

A. Method

The flowing afterglow apparatus used in these studies is basically that described previously,¹⁸ but some modi-

fications have been made. First, a lens system (Extranuclear) has been added. This lens system mounts onto the front of the quadrupole mass filter, and collects and collimates the ions from the high pressure source. It is located in the first of two differentially pumped chambers, where the pressure is typically 10⁻⁵ Torr. Addition of the lens system has greatly enhanced the ion signals seen, with the number of ion counts increasing more than an order of magnitude over the number of counts detected in the absence of the lenses. Second, the quadrupole itself has been moved into the second of the two differentially pumped chambers. Here pressures are on the order of 10⁻⁷ Torr. Placement of the quadrupole in this chamber substantially reduces chemical contamination of the quadrupole. Finally, refrigerated traps have replaced the water cooled baffles which separated the diffusion pumps from the two differentially pumped chambers. This decreases contamination of the system due to backstreaming of diffusion pump oil. Figure 1 is a schematic of the flowing afterglow apparatus, and it incorporates the modifications discussed above.

The flow tube was operated within a pressure range of 0.2–0.9 Torr (as measured by an MKS Baratron capacitance manometer) for the experiments presented here, and the buffer gas used was helium in all cases. The helium is passed through a molecular sieve maintained at 77 K, thus trapping out any condensible impurities such as H_2O , N_2 , and O_2 . Typically, the helium flow through the tube was 180 atm cm³ s⁻¹. All gas flows were measured with calibrated linear mass flow meters.

Source gases for all reactant ions except CF_4 were obtained from commercial suppliers and used without further purification. CF_4 commercially obtained was found to have some CF_3Cl impurity. Cooling the cylinder in a dry ice/acetone bath lowered the gas phase percentage of CF_3Cl somewhat. At high (~1 atm cm³ s⁻¹) flows of CF_4 , however, the amount of CF_2Cl^+ produced was larger than the amount of CF_3^+ produced, making it



FIG. 1. Schematic of modifications to flowing afterglow apparatus.

impossible to obtain reliable data on the reaction of CF_3^* with SF_6 under conditions of high CF_4 flow.

Reactant ions were produced by letting He^{*} ions react with the appropriate neutral gas. In the case of SF₆, reaction with He^{*} produces SF₃^{*}, SF₄^{*}, and SF₅^{*} with SF₃^{*} being the predominant species. When it was desirable to have SF₅^{*} as the major ion, He^{*} was first reacted with N₂ to produce a mixture of N^{*} and N₂^{*}. The N^{*}, N₂^{*} was then allowed to react with SF₆, and the energetics are such that SF₅^{*} is produced exclusively.

Because Kr reacts only slowly if at all with He^{*}, $k \le 10^{-11}$, ¹⁹ the above method for producing Kr^{*} was not satisfactory. The system of interest was the charge exchange between Kr^{*} and SF₆, and we could not afford to have He^{*} present in this system since it is definitely a source of SF₅ production. Therefore, the electron gun was maintained at <20 eV in order to minimize He^{*} formation [I. P. (He^{*}) = 24. 6 eV²⁰], and Kr^{*} ions were formed both by Penning ionization of neutral Kr by He metastables and by direct electron bombardment.

B. Treatment of data

Because reactant neutral concentrations were much larger than reactant ion concentrations, pseudo-first-order conditions obtain. Thus, for a reaction $A^* + B$ - products, the reaction ion concentration at some point z downstream from the introduction of B is given by^{21,22}

$$(\mathbf{A}^{\star}) = (\mathbf{A}^{\star})_{0} \exp\left[-\left(\frac{\beta D^{a}}{r^{2}} + \frac{k\mathbf{B}}{\alpha}\right) \frac{z}{\overline{v}}\right]$$

where α and β are constants, 1.6 and 3.67, respectively; r is the radius of the flow tube; D^a is the ambipolar diffusion coefficient of A^* ; \overline{v} is the bulk flow velocity, and k is the observed rate constant. For fixed \overline{v} and z, as the concentration of B is varied, one obtains

$$\ln \frac{(\mathbf{A}^{*})_{1}}{(\mathbf{A}^{*})_{2}} = \frac{kz}{\alpha \overline{v}} \left[(\mathbf{B})_{2} - (\mathbf{B})_{1} \right]$$

and plots of $ln(A^*)$ as a function of (B) are linear, with k obtainable from the slope of the line. For each kinetic run, a plot of log ion signal versus flow of neutral reactant B is made, and k is calculated from the slope.

An analysis of the equations characteristic of reactant ion loss for equilibria of the type $A^* + B \stackrel{-}{\rightarrow} C^* + D$ has been carried out.²³ The equilibrium constant K for such a process can be expressed as

$$K = \frac{(\mathbf{C}^*)}{(\mathbf{A}^*)} \frac{F_{\mathbf{D}}}{F_{\mathbf{B}}}$$

where F_B and F_D are flow rates of the neutrals B and D. According to this equation, then, under equilibrium conditions, a plot of the ion ratio $(C^*)/(A^*)$ as a function of neutral reactant flow F_B will be linear with slope K/F_D . We have accounted for any mass discrimination between the ions A^{*} and C^{*} by calculating a mass discrimination factor according to the method of Bohme *et al.*²³ The mass discrimination factor determined in our experiments was about 2. However, the exact value was very dependent upon the mass spectrometer control settings.

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Method	$\% SF_3^+$	% SF4	% SF ₅ ⁺	Reaction
Photoionization (21 eV) ^a	11	9	80	$h\nu + \mathrm{SF}_6 \rightarrow \mathrm{SF}_5^+ + \mathrm{F} + e^-$
Electron impact (70 eV) ^b	15	- 3	83	$e^{-} + SF_{6} \rightarrow SF_{5}^{+} + F + 2e^{-}$
He*, He*, 100 V°	75	14	33	$He^* + SF_6 \rightarrow SF_5^* + F + He, etc.$
He*, He*, 30 V	50	5	45	
He*, He*, 25 V	8	8	84	

TABLE I. Fragmentation patterns of SF₆.

^aReference 15. ^bReference 24.

^cVoltage refers to the energy of electron impact upon He neutral producing a mixture of He^{*} and He^{*}. The ratio of He^{*} to He^{*} increases as the voltage is lowered.

III. RESULTS AND DISCUSSION

A. Fragmentation of SF₆ by He⁺

We have studied the fragmentation pattern of the reaction $SF_6 + He^*$ at low flows of SF_6 . Table I shows the relative abundances of SF_3^* , SF_4^* , and SF_5^* produced and compares them to the relative abundances of these ions produced by photoionization at 21 eV^{15} and by electron impact at 70 eV.²⁴ While the photoionization and electron impact methods yield similar results, the fragmentation by He⁺ ions produces quite a different distribution of SF_3^* , SF_4^* , and SF_5^* . However, in common with previous results, we observed little if any SF^{*}₆, indicating that the ionization of SF_6 by a heavy particle collision must proceed through the same unstable SF^{*}₆ intermediate. In the case of $SF_6 + He^*$, the predominant ion formed is SF_3^* rather than SF_5^* . If the energy of the electron gun producing the helium afterglow is reduced, the ratio of He* to He* increases. The fragmentation patterns produced at lower energies (where the concentration of

He* is enhanced) show SF_5^* to be the major ion as in the photoionization and electron impact cases. In the fragmentation by He^{*}, all of the 24.6 eV of energy contained in the He^{*} ion is deposited in the SF₆ molecule. In the electron bombardment and photoionization experiments, the product electrons remove substantial amounts of energy from the excited complex. In addition, in electron bombardment the incident electron may scatter and carry away some of the energy so that only a portion is deposited in the SF₆ molecule upon impact. Thus the more severe fragmentation pattern is reasonable for fragmentation by He^{*} since the total energy of 24.6 eV is transferred to SF₆.

B. Reactions of SF₆ with some positive ions

The rate constants for the reactions of several positive ions with neutral SF_6 have been measured in the flowing afterglow. These are presented in Table II. The expected exothermicities or endothermicities

TABLE II. Reactions of SF_6 with positive ions M^* .

	A.P. $(SF_5^*/SF_6) - I.P.$ (M)	k ^b	k ^c
Reaction ^a	eV	cm molecule ⁻¹ s ⁻¹	
$SF_{6}^{+} He^{+} \rightarrow \begin{cases} SF_{5}^{+} + F + He \\ SF_{4}^{+} + 2F + He \\ SF_{3}^{+} + 3F + He \end{cases}$	- 10.18	2.0×10 ⁻⁹	2.0×10-9
$SF_6 + N_2^* \rightarrow SF_5^* + F + N_2$	-1.16	1.3×10-9	1.3×10-9
$SF_6 + N^+ \rightarrow SF_5^+ + NF$	-0.11	1.4×10-9	1.4×10^{-9}
$SF_6 + CO_2^* \rightarrow SF_5^* + CO_2F$	+0.65	1.4×10 ⁻¹¹	•••
$SF_6 + SO_2^{\bullet} \rightarrow SF_5^{\bullet} + SO_2F$	+2.08	2.8×10^{-10}	
$SF_6 + SO^* \rightarrow SF_5^* + SOF$	+4.25	4.5 \times 10 ⁻¹⁰	•••
SF ₆ + H ₃ O* -//		< 5×10 ⁻¹²	•••
$SF_6 + NO_2^* - // \rightarrow$	+4.67	< 5×10 ⁻¹²	•••
$SF_6 + NO^+ - // \rightarrow$	+5.16	< 5×10 ⁻¹²	<1×10 ⁻¹¹

^aThe product ion in all cases except He⁺ is SF₅⁺. For reactions which would be endothermic in the absence of bond formation, supposed neutral products are shown. Where A. P. (SF_5^+/SF_6) – I. P. (M) is negative, bond formation in the products may be present although it is not required by the energetics, and plausible neutral products are indicated. ^bThis work.

^eReference 17.

in the absence of any bond formation in the products are also indicated. Supposed neutral products are shown. The reactions of SF_6 with He⁺, N⁺, N₂⁺, and NO⁺ have been measured previously by Fehsenfeld, ¹⁷ and our results for these reactions agree extremely well with his (see Table II). For the reactions of SF₆ with CO⁺, SO⁺, and SO⁺, the energetics require that there be some bond formation in the products since A. P. $(SF_5^*/SF_6) - I$. P. (M) is positive in all cases and since the product ion observed is SF₅. Alternatively, the reactant ions could be in an excited or metastable state and, thus, lead to a reaction in which product bond formation is not required. However, the reactant ions are subject to several thousand collisions with helium before entering the reaction zone, so we assume that the reactant ions are in their ground state. Should a small fraction of the reactant ions be in a metastable state, and only that state is responsible for reaction, the derived rate constant would be anomalously small. Thus, we have indicated neutral products in which a bond to fluorine has been formed, although we have no experimental method of determining the identity of these neutral products.

C. $CF_3^+ + SF_6 \rightleftharpoons SF_5^+ + CF_4$

In investigating the reaction of the CF_3^+ ion with SF_6 ,



FIG. 2. Plot of CF_3^* ion signal decay and SF_5^* ion signal growth as a function of SF_6 flow. P=0.709 Torr and $F_{CF_4}=0.690$ atm cm³s⁻¹. Sharp curvature indicates equilibrium in the system.



FIG. 3. Plot of product ion to reactant ion ratio for $CF_3^++SF_6$ $\Rightarrow SF_5^++CF_4$ as a function of SF_6 flow. P=0.709 Torr and F_{CF_4} = 0.690 atm cm³ s⁻¹. The linear portion of the curve represents the attainment of equilibrium, and gives $K = 6.6 \times 10^3$ when the mass discrimination factor is applied.

it was seen that plots of $log(CF_3^*)$ vs SF₆ flow showed significant curvature at high flows of SF_6 . This behavior can be indicative of a reaction in which an equilibrium is established. Because the CF_3^+ ion was produced from CF_4 , there were large amounts of CF_4 in the system and it was possible to be in the regime where significant back reaction set up the equilibrium situation. Figure 2 shows a graph of $log(CF_3^*)$ as a function of SF_6 concentration, and the curvature due to the establishment of an equilibrium can clearly be seen. The results of the kinetic runs are plotted as described in the experimental section, and graphs of the type shown in Fig. 3 are obtained. The linear portion of the curve represents the reaction in its equilibrium state, and an equilibrium constant K can be extracted from the slope. Several runs were carried out varying the flow tube pressure from 0.2 to 0.9 Torr and varying the flow of CF_4 from 0.1 to 1 atm cm³ s⁻¹. The results are tabulated in Table III. The average equilibrium constant calculated from these data is 5.9×10^3 . Although the equilibrium constant calculated is conservatively stated to be $\pm 50\%$, this variation has little effect upon the calculation of ΔG° for the reaction (the thermodynamic parameter crucial to the following calculations). The variation of $\pm 50\%$ in K is reflected in an uncertainty in ΔG° of only ± 0.01 eV. At 298 K, ΔG° is calculated to be -0.22 ± 0.01 eV.

In order to obtain ΔH° for the reaction, one must calculate the change in entropy for the reaction

TABLE III. Equilibrium constant calculations $CF_3^* + SF_6^{==} SF_5^* + CF_4$.

F_{CF_4} , 10 ⁻³ atm cm ³ s ⁻¹	P (Torr)	K	$-RT\ln K$ at 298
95	0.500	6.0×10^{3}	-0.22 eV
95	0.702	4.8×10^{3}	-0.22 eV
690	0.501	5.2×10^{3}	-0.22 eV
690	0.709	6.6×10^{3}	-0.23 eV
690	0.893	5.6×10^{3}	-0.22 eV
983	0.710	7.3 $\times 10^{3}$	-0.23 eV

$$CF_3^* + SF_6 - SF_5^* + CF_4$$
.

Entropies of CF₃^{*}, SF₆, and CF₄ are as follows: S₂₉₈[°](CF₃^{*}) = 60.8 ± 0.4 gibbs/mol, ²⁶ S₂₉₈[°](SF₆) = 69.7 ± 0.1 gibbs/ mol, ²⁵ S₂₉₈[°](CF₄) = 62.45 ± 0.06 gibbs/mol.²⁷ The entropy of SF₅^{*} is assumed to be that of PF₅, 71.19 ± 0.5 gibbs/ mol.²⁷ From this at 298 K, *T*\DeltaS is calculated to be 0.05 ± 0.01 eV. Using the relationship $\Delta H_T^\circ = \Delta G_T^\circ + T\Delta S_T^\circ$, ΔH_{298}° is found to be $- 0.17 \pm 0.02$ eV.

A derivation of the CF₃-F bond strength from heats of formation yields 129.6±1 kcal/mol or 5.62±0.04 eV. The heats of formation used are $\Delta H_{298}^{\circ}(CF_4) = -223.0 \pm 0.3 \text{ kcal/mol}, ^{27} \Delta H_{298}^{\circ}(CF_3) = -112.4\pm1 \text{ kcal/mol}, ^{27}$ and $\Delta H_{298}^{\circ}(F) = 18.97\pm0.07 \text{ kcal/mol}.^{28}$ The ionization potential of CF₃ has been reported as 9.17±0.08 eV.²⁹ Using these values and the value of ΔH_{298}° calculated above, one can set up the following thermochemical cycle:

$SF_6 \rightarrow SF_5^* + F + e^-$,	A. P. (SF_5^*/SF_6) ,
$e^- + \operatorname{CF}_3^* - \operatorname{CF}_3$,	$-9.17 \pm 0.08 \text{ eV}$,
$CF_3 + F - CF_4$,	$-5.62 \pm 0.04 \text{ eV}$,
$CF_3^* + SF_6 \rightarrow SF_5^* + CF_4$	$-0.17 \pm 0.02 \text{ eV}$.

The appearance potential of SF_5^+ from SF_6 as calculated from this cycle is 14.62±0.09 eV. This is significantly lower than the appearance potentials 15.29 eV (photoionization), ¹⁵ 15.35 eV (photoelectron spectroscopy), ¹⁶ and 15. 50 eV (electron impact)^{11(c)} measured previously.

As an independent method of obtaining A. P. (SF_5^*/SF_6) , we looked at the $Kr^* + SF_6$ charge exchange reaction. The ionization potential to produce $Kr^*({}^2P_{3/2})$ is 14.00 eV, while that to produce $Kr^*({}^2P_{1/2})$ is 14.68 eV.²⁹ Thus, if the reaction $Kr^* + SF_6 - SF_5^* + Kr + F$ proceeds, one can conclude that A. P. $(SF_5^*/SF_6) \le I$. P. (Kr), and an upper limit for the appearance potential can be set. The charge exchange reaction does indeed take place, and so A. P. $(SF_5^*/SF_6) \le 14.68 \text{ eV}.$

When Kr⁺ ions are formed as described in the experimental section, both the ${}^{2}P_{1/2}$ and the ${}^{2}P_{3/2}$ states are produced. Other flowing afterglow work has shown it to be likely that ions in the ${}^{2}P_{1/2}$ state are de-excited to the ${}^{2}P_{3/2}$ state before reaching the reaction region.³⁰ We performed qualitative experiments to determine which state was causing SF⁺₅ production. Keeping the point of addition of krypton gas fixed at the ion inlet port, we added SF⁺₆ either at the upstream neutral inlet (closer to the Kr inlet) or at the downstream neutral inlet (further

from the Kr inlet). The SF^{*}₅ ion signal was monitored in both cases, and we saw smaller signals when SFs was added at the downstream neutral inlet. The additional distance between Kr⁺ production and SF₆ introduction in this case where SF_6 is added further from the Kr inlet allows the relaxation of $\operatorname{Kr}^{*}({}^{2}P_{1/2})$ to $\operatorname{Kr}^{*}({}^{2}P_{3/2})$ to proceed to a greater extent. The smaller SF^{*}₅ signal under these conditions leads us to believe that $Kr^{*(2}P_{1/2})$ at 14.68 eV gives the SF_5^* . Helium ion blanks with SF_6 were run under the same conditions, and we determined that in the case of the $Kr^* + SF_6$ reaction, the decrease in ion signal was larger than that expected due to diffusional losses of reactant ion. Thus, relaxation of $\operatorname{Kr}^{*}({}^{2}P_{1/2})$ to $\operatorname{Kr}^{*}({}^{2}P_{3/2})$ has probably occurred, and the charge exchange reaction with SF₆ most likely involves the ${}^2P_{1/2}$ state of Kr⁺. In any event, if the state responsible for producing SF_5^* cannot be identified unambiguously as $Kr^{*(2}P_{1/2})$ at 14.68 eV or $Kr^{*(2}P_{3/2})$ at 14.00 eV, the same upper limit A. P. $(SF_5^*/SF_6) \le 14.68$ eV would be set. That this limit is also substantially lower than previously published values of A. P. (SF_5^*/SF_6) supports our conclusion from the equilibrium study that A. P. (SF_5^*/SF_6) is 14.62 eV.

The forward rate constant for the $CF_3^* + SF_6 \rightarrow SF_5^*$ + CF_4 reaction was determined by two methods. First, CF_3^* was produced from CF_4 , but CF_4 flows used were low enough such that equilibrium conditions did not obtain. Second, CF_3^* ions were produced from the reaction of He^{*} ions with $(CF_3)_2CO$. Because there was never a large amount of the neutral product CF_4 present, there was no possibility of equilibrium being established in this second case. Both methods gave values of k_f = $(2.5 \pm 0.2) \times 10^{-10}$ cm³ mol⁻¹ s⁻¹. The error here indicates the reproducibility of measurements of k_f . We estimate the overall uncertainty of the rate constant to be $\pm 30\%$.

The equilibrium system involving CF_3^* and SF_5^* provided an interesting study to validate the three ion concentration dependent diffusion model developed by Streit and Newton.³¹ While this system does involve large polyatomic ions, the ratio of product ion to reactant ion free diffusion coefficients is smaller than in those systems studied previously, so it was not certain that concentration dependent changes in diffusion loss would be significant. The model was readily modified by adding a back reaction term to the differential equation.

For calculation purposes the diffusion coefficients of CF_3^* , SF_5^* , and the counter ion F⁻ were needed. The diffusion coefficient of F⁻ in He has been determined³² to be 628 cm² Torr s⁻¹. The diffusion coefficients of CF_3^* and SF_5^* were assumed by analogy with CO_3^- and SF_5^- to be 365 and 291 Torr s⁻¹, respectively. ³³ To determine whether changes in diffusion as a function of concentration were significant, two types of calculations were made. In the first set of calculations the diffusion coefficients of CF_3^* and SF_5^+ were fixed during the course of the reaction. That is, each ion had a unique and constant ambipolar diffusion coefficient based on its free diffusion coefficient and that of F⁻. In this type of calculation, the equilibrium constants which best fit the

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data were invariably approximately 50% lower than those values determined graphically directly from the data.

In the second type of calculation, the ambipolar diffusion coefficients of CF_3^* and SF_5^* were assumed to be a function of concentration and, thus, were not constant during the course of the reaction. The best fit equilibrium constants determined from these calculations agreed with the graphical determinations within 5%. These results indicate again that in flowing afterglow studies involving large polyatomic ions, usually with relatively small diffusion coefficients, the dependence of diffusion loss on extent of reaction complicates straightforward interpretation of the data.

D. Ionization potential of SF₅

The appearance potential of SF_5^* from SF_6 can be expressed as the sum of I. P. (SF_5) and $D_{298}(SF_5-F)$:

$$SF_{6} \rightarrow SF_{5} + F , \quad D(SF_{5} - F) ,$$

$$SF_{5} \rightarrow SF_{5}^{+} + e^{-} , \quad I. P. (SF_{5}) ,$$

$$SF_{6} \rightarrow SF_{5}^{+} + F + e^{-} , \quad A. P. (SF_{5}^{*}/SF_{6}) .$$

We have studied a series of charge exchange reactions of the type $SF_5^* + M - M^* + SF_5$ in order to determine a value of I. P. (SF_5) . The results are summarized in Table IV. The detection of M^* and the loss of SF_5^* were taken to indicate charge exchange, and it was interpreted to mean I. P. $(SF_5) \ge I. P. (M)$. In the case of $H_2S + SF_5^*$, the product ion observed is H_3S^* . However, the reaction $H_2S + H_2S^* - H_3S^* + HS$ has been reported³⁴ to proceed with a rate constant of 5. 8×10^{-10} cm³ molecule⁻¹ s⁻¹, so we conclude that H_3S^* formation is preceded by H_2S^* formation, and that charge exchange has in fact taken place. Rate constants (or upper limits) for the reactions studied are also presented in Table IV. The ionization potential of SF₅ based upon examination of these charge exchange reactions is 10.5 ± 0.1 eV. This is within the limits 9.25 \leq I. P. \leq 12.05 eV established by Fehsenfeld. 17

Using this value of I. P. (SF_5) and the value of A. P. (SF_5^*/SF_6) obtained from our equilibrium studies, a bond dissociation energy of 4.1 ± 0.13 eV is calculated for the SF_5 -F bond. This value is higher than values reported by Hildenbrand^{11(c)} and by Bott and Jacobs, ^{11(b)} but is in excellent agreement with the value calculated by Lyman¹² and with that measured by Kiang and Zare. ¹⁴ Ours is the only experimental measurement besides that of Kiang and co-workers which yields a value close to 4 eV.

IV. SUMMARY AND CONCLUSIONS

The fragmentation pattern for the reaction of SF_6 with He⁺ has been reported. Because of the energetics involved, SF_3^* is the major ion produced. This is in contrast to the fragmentation patterns produced by photoionization and by photoelectron spectroscopy, where the predominant ion is SF_5^* . The use of the flowing afterglow to study fragmentation patterns allows the amount of energy transferred to be unambiguously known. In the case of He⁺ + SF_6, all 24. 6 eV contained in the He⁺ ion is deposited in the SF_6 molecule.

By studying the $CF_3^* + SF_6^- \Rightarrow SF_5^* + CF_4$ equilibrium, we have determined the appearance potential of SF_5^* from SF_6 to be 14.62 eV. Derivation of the appearance potential via the equilibrium system yields an adiabatic value. Previous measurements by electron impact and photoionization techniques yield vertical transition appearance potentials which are frequently at higher energy than the adiabatic transition. In this case, our value is approximately 1 eV lower than previously reported values.

Charge exchange reactions of SF_5^* with molecules of known ionization potentials were examined, and lead to a value of I. P. $(SF_5)=10.5\pm0.1$ eV. Combining this new value with A. P. $(SF_5^*/SF_6)=14.62$ eV as determined above yields a bond dissociation energy of 4.1 eV for the SF_5-F bond. This is in excellent agreement with the experimental value obtained by chemiluminescence, ¹⁴ and is the only other experimental conformation of the theoretical value obtained using RRKM theory. ¹²

Finally, a comment can be made on the SF_4 -F bond energy. The reaction of SF_5^* with HI was found to be as follows:

$$SF_5^* + HI \rightarrow SF_4 + HF + I^*$$
.

If $D_{298}^{\circ}(SF_4-F)$ is taken as 3.12 eV as reported by Hildenbrand, ^{11(c)} then the reaction is predicted to be thermodynamically unfavorable. However, if $D_{298}^{\circ}(SF_5-F)$ is taken as 4.1 eV, and $D_{298}^{\circ}(SF_4-F)$ is then recalulated using Hildenbrand's values of I. P. (SF_4) and ΔH for SF_6 $\rightarrow SF_4 + 2F + 2e$, then one arrives at an energy of 2.4 eV for the SF_4-F bond. This value is also in very close agreement to the recent chemiluminescence results.¹⁴ If this number is used in calculating the thermochemical cycle for the SF_5^* + HI reaction as written above, the production of SF_4 + HF + I* becomes thermodynamically favorable.

In presenting new values for I. P. (SF_5) , A. P. (SF_5')

TABLE IV. Reactions of SF_5^* with various neutrals M.

М	I.P. (M) eV	Reaction	$k \operatorname{cm}^3 \operatorname{mol}^{-1} \operatorname{s}^{-1}$	I.P. (SF ₅) limit eV
NO ₂	9.75	$SF_5^+ + NO_2 \rightarrow NO_2^+ + SF_5$	2.3×10 ⁻¹¹	I. P. $(SF_5) \ge 9.75$
NH3	10.17	$\mathbf{SF}_5^{\star} + \mathbf{NH}_3 \rightarrow \mathbf{NH}_3^{\star} + \mathbf{SF}_5$	1.2×10-9	I. P. $(SF_5) \ge 10.17$
H_2S	10.43	$\mathbf{SF}_5^{\bullet} + \mathbf{H}_2 \mathbf{S} \xrightarrow{\bullet} \mathbf{H}_2 \mathbf{S}^{\bullet} + \mathbf{SF}_5$	5.6×10 ⁻¹¹	I. P. $(SF_5) \ge 10.43$
Br_2	10.51	$\mathbf{SF}_5^{\bullet} + \mathbf{Br}_2 \rightarrow \mathbf{Br}_2^{\bullet} + \mathbf{SF}_5$	<4×10 ⁻¹²	I. P. $(SF_5) \le 10.51$
Cl ₂	11.48	$\mathbf{SF}_5^+ + \mathbf{Cl}_2 \mathbf{Cl}_2^+ + \mathbf{SF}_5$	<4×10 ⁻¹²	I. P. $(SF_5) \le 11.48$

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 SF_6), and $D^{\circ}_{298}(SF_5-F)$ and in reporting the 24.6 eV fragmentation pattern for SF_6 , we have demonstrated the versatility of the flowing afterglow technique. Photoionization, photoelectron spectroscopy, and the various electron impact techniques have the associated problem that it is often difficult to extract adiabatic information. Unless the geometry of the ion and its internuclear distances are quite similar to those in the neutral molecule, several vibrational states of the ion will be accessible through the vertical ionization process. It may be very difficult to extract the adiabatic ionization potential from the series of Franck-Condon allowed transitions. In addition to Franck-Condon factors, hot bands, autoionization, and fragmentation can also complicate interpretation of data from these techniques. Because of the large amounts of buffer gas used in the following afterglow method, all processes are thermalized. The charge exchange reactions and the thermochemical fragmentation are room temperature processes and represent adiabatic transition. Thus, flowing afterglow data is not plagued by the problems mentioned above, and the I. P.'s and A. P.'s determined are indeed adiabatic. This work has pointed out that in addition to being a convenient method for obtaining rate constants of ion-molecule reactions, the flowing afterglow is also a valuable tool for obtaining thermochemical parameters.

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