A Selected Ion Flow Tube Study of the Reactions of Several Cations with the Group 6B Hexafluorides SF_6, SeF_6, and TeF_6

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The first investigation of the ion chemistry of SeF_6 and TeF_6 is presented. Using a selected ion flow tube, the thermal rate coefficients and ion product distributions have been determined at 298 K for the reactions of 14 atomic and molecular cations, namely, H_3O^+, CF_3^+, CF^+, CF_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, CO^+, N^+, N_2^+, Ar^+, F^+, and Ne^+ (in order of increasing recombination energy), with SeF_6 and TeF_6. The results are compared with those from the reactions of these ions with SF_6, for which the reactions with CF^+, CF_2^+, N_2O^+, and F^+ are reported for the first time. Several distinct processes are observed among the large number of reactions studied, including dissociative charge-transfer and F^-, F, F_2^-, and F_2 abstraction from the neutral reactant molecule to the reagent ion. The dissociative charge-transfer channels are discussed in relation to vacuum ultraviolet photoelectron and threshold photoelectron−photoion coincidence spectra of XF_6 (X = S, Se, or Te). For reagent ions whose recombination energies lie between the first dissociative ionization limit ($XF_6 \rightarrow XF_5^+ + F + e^-$) and the onset of ionization of the XF_6 molecule, the results suggest that if dissociative charge-transfer occurs, it proceeds via an intimate encounter. For those reagent ions whose recombination energies are greater than the onset of ionization, long-range electron transfer may occur depending on whether certain physical factors apply, for example, nonzero Franck−Condon overlap. From the reaction kinetics, limits for the heats of formation (in kJ mol^{-1}) of SeF_4, SeF_5, TeF_4, and TeF_5 at 298 K have been obtained: $\Delta_f H°(SeF_4) < -369$, $\Delta_f H°(SeF_5) < -621$, $\Delta_f H°(TeF_4) > -570$, and $\Delta_f H°(TeF_5) < -822$.

1. Introduction

There have been a number of studies investigating the reactions of various cations with SF_6.[1−6] These studies have been explorations of fundamental ion−molecule chemistry[1−4] and have addressed important questions in applied sciences, such as the possible effects of ion reactions on the atmospheric lifetime of SF_6 and the use of SF_6 in industrial plasma processes.[5,6] In contrast, no information is available on the positive-ion chemistry of the homologous molecules SeF_6 and TeF_6. Here, we report the first study of the positive-ion chemistry of SeF_6 and TeF_6. An objective of this study is to explore the nature of the reaction ion chemistry as the central atom in a hexafluoride molecule is changed. Differences in the reaction dynamics and kinetics may shed light on the ion chemistry occurring in SF_6-containing plasmas.[6] Furthermore, this study is of fundamental interest in the interpretation and understanding of ion−molecule reactions.

In this paper, the thermal (298 K) reactions of 14 ions spanning a range of recombination energies (6.37−21.56 eV), namely (in order of increasing recombination energy), H_3O^+, CF_3^+, CF^+, CF_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, CO^+, N^+, N_2^+, Ar^+, F^+, and Ne^+, with SeF_6 and TeF_6 are presented. In addition, the reactions of CF^+, CF_2^+, N_2O^+, and F^+ with SF_6 have been investigated for the first time. Reaction rate coefficients and product ion distributions are reported. For completeness and ease of comparison, the reactions of the other ions with SF_6, which have been previously studied,[1−6] are presented here. Of these, the reactions of H_3O^+, CF_3^+, CO_2^+, CO^+, N_2^+, Ar^+, and Ne^+ with SF_6 have been reinvestigated in this study, and here there is good agreement in both the rate coefficients and the product ion branching ratios with those obtained in the other studies.

The large range of recombination energies of the reagent ions used in this study ensures that varied and interesting reactions occur. For example, charge (electron) transfer will only be energetically possible for those ions having recombination energies greater than the first dissociative ionization limit of the XF_6 molecule (X = S, Se, or Te), $XF_6 \rightarrow XF_5^+ + F + e^-$. The first dissociative ionization limit is used because threshold photoelectron−photoion coincidence (TPEPICO) studies show that the ground state of XF_6^+ is not a stable ion and dissociates to $XF_5^+ + F$.[7,8] (Any bound region of the XF_6^+ potential energy surface lies well outside that accessible from the neutral XF_6 ground state.) Even when (dissociative) charge-transfer is energetically possible, this constraint does not necessarily guarantee that it will occur. Other reaction processes might explain the observed product ions, providing that an intimate encounter of the reagent ion with the neutral molecule takes place. An intimate (short-range) encounter must take place for the reactions of those ions for which charge-transfer is energetically impossible. Furthermore, chemical reactions in which bonds are broken and formed might occur, such as fluorine abstraction. Examples of all the reaction processes referred to above are evident in this study and will be discussed in section 3.

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2. Experiment

A selected ion flow tube (SIFT) was used to measure rate coefficients and to record product ions of the reactions. The SIFT apparatus and its mode of operation have been described in detail previously,[9,10] so only a brief description is required here. The reagent ions were generated in an enclosed electron impact high-pressure ion source containing an appropriate gas (Ne for Ne^+, CF_4 for F^+, Ar for Ar^+, N_2 for N_2^+ and N^+, CO for CO^+, CO_2 for CO_2^+ and O^+, N_2O for N_2O^+, H_2O for H_2O^+ and H_3O^+, and C_2F_6 for CF_2^+, CF^+, and CF_3^+). The reagent ions were mass selected using a quadrupole mass spectrometer, injected into a 298 K helium carrier gas at a pressure of ~0.5 Torr, transported along the flow tube, and detected by a downstream sampling orifice/mass spectrometer detection system. Reactant neutral molecules were added in controlled amounts to the ion swarm/carrier gas, and the loss of reagent ions and the appearance of product ions were monitored by the downstream detection system. The reaction rate coefficients and ion product distributions were then determined in the usual way[9−11] and are considered to be accurate to ±20%.

The high pressure of the gases in the ionization source is expected to significantly quench (metastable) electronically and vibrationally excited states of many molecular ions prior to their injection into the flow tube, and it is assumed that the ions are thermalized in the helium carrier gas. We have not made any independent checks to confirm whether these assumptions are correct, other than for N_2^+. For this reagent ion, we know from a previous study that a significant fraction of the N_2^+ ions in the flow tube was vibrationally excited (~40% in $v = 1$).[12] Although it is possible that other reagent molecular ions have internal energies above thermal, no curvature was observed in any of the pseudo-first-order kinetic plots (logarithm of the reagent ion signal vs the reactant neutral concentration). This indicates that rate coefficients are the same for reactions involving ground and any vibrationally excited states. This does not rule out reagent ion vibrational excitation influencing the ion product distributions for those reactions which produce more than one ion product.

Atomic ions are expected to be in their ground electronic states prior to reaction with a neutral molecule. The Ar^+ and Ne^+ ions should emerge from the high-pressure source in their ground electronic state, $^2P_{3/2}$. Even if this were not the case, the energy separation between the $^2P_{3/2}$ and $^2P_{1/2}$ states is only 0.18 eV for Ar^+ and 0.10 eV for Ne^+, and therefore differences in reactivities between the two spin−orbit states are not expected. No evidence was found for differences in their reaction rates. Whether differences in branching ratios result from reactions involving these two spin−orbit states is more difficult to assess, but given the small differences in energy, none are expected. The ground state of F^+ is a closely spaced triplet with recombination energies of 17.42 ($^3P_2$), 17.47 ($^3P_1$), and 17.48 eV ($^3P_0$). Thus, for this ion there will be significant population in all three states. As for Ar^+ and Ne^+, no differences in the reactivity of the F^+ ion in its various spin−orbit states are to be expected. For the other two atomic ions used in this investigation, electronically excited states of N^+ and O^+ have previously been shown not to be present.[12]

Water contamination in the flow tube resulted in electron transfer from H_2O to those injected ions whose recombination energies are greater than the ionization potential of H_2O, 12.61 eV. The resulting H_2O^+ signal was always less than 3% of the parent ion signal. Some of the H_2O^+ was converted to H_3O^+ in the flow tube via reaction pathway 1.

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \qquad (1)$$

Fortunately, the reactions of H_2O^+ and H_3O^+ with any of the three group 6B hexafluorides of this study are either insignificant or slow. In any case, the reactions of H_2O^+ with SF_6 and TeF_6 and of H_2O^+ and H_3O^+ with SeF_6 caused no difficulty in assigning the product ions for the reaction involving the parent reagent ion. Slightly more problematic in the data analysis was the reaction of Ne^+ with trace H_2O, which resulted in impurity ion signals of OH^+ and H_2O^+ in the flow tube at a level of about 5% and 3%, respectively, of that of Ne^+ via dissociative and nondissociative charge-transfer:

$$Ne^+ + H_2O \rightarrow OH^+ + H + Ne \qquad (2a)$$

$$\rightarrow H_2O^+ + Ne \qquad (2b)$$

In addition to these two ion products, $HeNe^+$ ions were formed in the flow tube from termolecular reactions of Ne^+ with the He buffer gas:

$$Ne^+ + 2He \rightarrow HeNe^+ + He \qquad (3)$$

This led to a $HeNe^+$ signal of about 2% of the Ne^+ signal. For the reasons given above, the reactions of H_2O^+ (from trace H_2O) with XF_6 (X = S, Se, or Te) do not need to be taken into account. We have not made any allowances for the reactions of $HeNe^+$ and OH^+ with the neutral molecules of this study. However, given the low percentage of these impurity ions, their contributions to the yields of the product ions for the Ne^+ reaction can reasonably be neglected.

Samples of the three compounds investigated in this study were purchased from Fluorochem Limited, Derbyshire, U.K., with the following stated purities: sulfur hexafluoride (>99%), selenium hexafluoride (99%), and tellurium hexafluoride (>99%). They were used directly without additional purification.

3. Results and Discussion

The experimentally recorded reaction rate coefficients, k_{exp}, the product ions, and their branching ratios are given in Tables 1−3 for SF_6, SeF_6, and TeF_6, respectively. The reagent ions are listed (top to bottom) in order of decreasing recombination energy (RE) in units of electronvolts (eV). Also presented in the tables are the calculated collisional rate coefficients, k_c, determined according to the Langevin equation for nonpolar molecules.[13] Input data to these calculations include the polarizability, α, of the neutral reactant molecule: $\alpha(SF_6) = 6.54 \times 10^{-24}$, $\alpha(SeF_6) = 7.33 \times 10^{-24}$, and $\alpha(TeF_6) = 9.00 \times 10^{-24}$ cm^3.[14]

The determination of reaction pathways requires knowledge of the ion and neutral products and their associated thermochemical data. Thus, an identification of both the ion and neutral products is ideally required. In our experiments, this is not possible because we can only measure the masses of the ion products and their relative intensities. Nevertheless, we can normally make some progress toward the above goal by invoking mass balance and thermochemical arguments. Consideration of the effects of enthalpy on the rate coefficients of reactions between thermalized reactants shows that, unless the reaction has $\Delta_r H° < 0$, k_{exp} will be less than k_c. Further, if $\Delta_r H° > 20$ kJ mol^{-1}, then at 298 K the reaction channel will be too slow for the ion product to be detected in our SIFT apparatus. In generating a list of possible pathways to an observed ion product, we normally exclude any pathway for which $\Delta_r H° >$

TABLE 1: Measured 298 K Reaction Rate Coefficients and Ion Product Branching Ratios for the Reactions of H_3O^+, CF_3^+, CF^+, CF_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, CO^+, N^+, N_2^+, Ar^+, F^+, and Ne^+ with SF_6[g]

			branching ratio (%)		reaction rate coefficient/ 10^{-9} cm^3 molecule^{-1} s^{-1}		
reagent ion	RE/eV	ion products	present	previous	present	previous	Langevin
Ne^+	21.56	SF_3^+	88	91[a]	0.69	0.78[a]	1.4
		SF_4^+	2	3			
		SF_5^+	10	6			
F^+	17.42	SF_3^+	10		1.10		1.5
		SF_5^+	90				
Ar^+	15.76	SF_5^+	100	100[b,c]	0.91	0.93,[b] 1.2[c]	1.1
N_2^+	15.58	SF_5^+	100	100[a,c,d]	1.03	1.2,[a] 1.3[c,d]	1.2
N^+	14.53	SF_3^+		2[a]		1.8,[a] 1.4[c,d]	1.7
		SF_5^+		98,[a] 100[c,d]			
CO^+	14.01	SF_5^+	100	100[c,e]	0.92	1.3,[c] 0.98[e]	1.2
CO_2^+	13.77	SF_5^+	100	100[d]	0.09	0.01[d]	1.0
O^+	13.62	SF_5^+		100[c,f]		1.5,[c] 2.4[f]	1.6
N_2O^+	12.89	SF_5^+	100		0.003		1.0
H_2O^+	12.61	$(OSF_4)^{+}$[a]				0.19[a]	1.5
		$(OHSF_5)^+$					
		$(H_2OSF_6)^+$					
CF_2^+	11.42	SF_5^+	100		0.79		0.98
CF^+	9.11	SF_5^+	95		0.88		1.2
		CF_3^+	5				
CF_3^+	≤ 8.8	SF_5^+	100	100[d]	0.22	0.25[d]	0.87
H_3O^+		no reaction				≤ 0.005[d] ≤ 0.002[a]	1.5

[a] Williams et al. (ref 6). [b] Shul et al. (ref 4). [c] Fehsenfeld (ref 1). [d] Babcock and Streit (ref 3). [e] Bowers and Chau (ref 2). [f] Morris et al. (ref 5). [g] The recombination energies (RE) in electronvolts (eV) of the reagent ions are listed. The reactions with N^+, O^+, H_2O^+, and H_3O^+ have not been investigated by us, but data for these reactions are presented for completeness (refs 1−6). The Langevin (collisional) rate coefficients have been calculated (ref 13) and are shown for comparison with the experimental values. The estimated uncertainty in the measured rate coefficients and the product ion branching ratios is ±20%.

0. This analysis is restricted to considerations of enthalpy, and we have ignored possible entropic effects.[15] Entropic factors will oppose the endothermicity for reactions in which there is an increase in the number of species between reactants and products, and we note that for most of the reactions in this study there is either no change or an increase of 1 or 2 species. However, entropy effects are likely to be significant only if the enthalpy change of a reaction is close to zero. In the text, errors in the enthalpies of reaction are given only for those which are close to thermoneutral.

SF_6 is an important molecule, used in industrial plasmas and as an insulator to inhibit high-voltage electrical breakdown. Thus, the thermochemistry of this molecule and its fragments in both neutral and cationic forms is reasonably well established.[16] The one exception is the enthalpy of formation of SF_5^+, for which a huge range of values spanning over 100 kJ mol^{-1} exists in the literature.[17] We use a value for $\Delta_f H°(SF_5^+)$ of 52 kJ mol^{-1}, corresponding to a dissociative ionization energy for $SF_6 \rightarrow SF_5^+ + F + e^-$ of 14.0 eV, for reasons explained elsewhere.[8,18] Our value is 41 kJ mol^{-1} higher than that quoted in the NIST website.[16] This difference, however, is not sufficient to change the sign of $\Delta_r H°$ for reactions producing SF_5^+ as the product ion. In other words, our interpretation of the mechanisms of reactions which form SF_5^+ is not dependent on which value of $\Delta_f H°(SF_5^+)$ is used. The heats of formation of the reagent ions are well established except for CF_3^+. The value of the ionization energy of the CF_3 radical, and hence $\Delta_f H°(CF_3^+)$, was reviewed recently,[19] and we use the value proposed there for $\Delta_f H°(CF_3^+)$ of +386 kJ mol^{-1}. With these two caveats, we can therefore calculate the enthalpy changes of all reactions involving SF_6.

By contrast, there is less information about the thermochemistry and ion energetics of SeF_6 and TeF_6. Potts et al. have recorded the vacuum ultraviolet photoelectron spectra (VUV PES) of SeF_6 and TeF_6,[20] and Addison et al. the VUV PES of SeF_6.[21] From these PES, the ionization potentials of various ionic states of SeF_6 and TeF_6 can be determined. However, such information is of limited use to analyze the ion chemistry of these molecules. Adiabatic ionization potentials, dissociative ionization limits, details on the decay mechanisms of the various ionic states, and enthalpies of formation of the fragment ions are all needed. To help with the analysis of this ion−molecule investigation, we have recently recorded TPEPICO spectra of SeF_6 and TeF_6.[8] From the data, dissociative ionization limits have been determined. Furthermore, heats of formation of SeF_3^+, SeF_4^+, SeF_5^+, TeF_3^+, TeF_4^+, and TeF_5^+ have been derived to be 368 ± 28, 426 ± 36, 166 ± 52, 380 ± 28, 428 ± 36, and 4 ± 62 kJ mol^{-1}, respectively. Together with $\Delta_f H°(SeF_6) = -1117 \pm 21$ and $\Delta_f H°(TeF_6) = -1318 \pm 21$ kJ mol^{-1},[22] these heats of formation have been used to calculate the enthalpies of various reaction pathways reported in this study. Dissociative ionization limits are used to determine if charge-transfer is energetically possible.

TPEPICO data are useful not only for determining thermodynamic information for the analysis of positive-ion charge-transfer data but also for comparing product ion branching ratios at energies consistent with the recombination energy of the reagent ion. Differences observed in the product ion branching ratios may indicate that a short-range ion−molecule reaction involving an intimate encounter, rather than a long-range electron jump, has occurred. The recent studies of the charge-transfer reactions of CCl_4 and SF_6[6] and of several saturated and

TABLE 2: Measured 298 K Reaction Rate Coefficients and Ion Product Branching Ratios for the Reactions of H_3O^+, CF_3^+, CF^+, CF_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, CO^+, N^+, N_2^+, Ar^+, F^+, and Ne^+ with SeF_6[a]

		SeF_6			
reagent ion	RE/eV	ion products	branching ratio (%)	reaction rate coefficient/10^{-9} cm^3 molecule^{-1} s^{-1}	
				present	Langevin
Ne^+	21.56	SeF_3^+	92	1.2	1.5
		SeF_5^+	8		
F^+	17.42	SeF_3^+	4	1.4	1.5
		SeF_5^+	96		
Ar^+	15.76	SeF_5^+	100	1.2	1.1
N_2^+	15.58	SeF_5^+	100	1.6	1.3
N^+	14.53	SeF_5^+	100	1.6	1.8
CO^+	14.01	FCO^+	52	1.1	1.3
		SeF_3^+	14		
		SeF_5^+	34		
CO_2^+	13.77	SeF_5^+	100	<0.01	1.1
O^+	13.62	SeF_5^+	100	1.5	1.6
N_2O^+	12.89	SeF_5^+	100	<0.01	1.1
H_2O^+	12.61	SeF_5^+	100	<0.05	1.6
CF_2^+	11.42	CF_3^+	52	0.93	1.0
		SeF_5^+	48		
CF^+	9.11	CF_3^+	74	0.64	1.2
		SeF_5^+	26		
CF_3^+	≤8.9	SeF_5^+	100	0.44	0.89
H_3O^+		? (see text)		<0.001	1.5

[a] The recombination energies (RE) in electronvolts (eV) of the reagent ions are listed. The Langevin (collisional) rate coefficients have been calculated (ref 13) and are shown for comparison with the experimental values. The estimated uncertainty in the measured rate coefficients and the product ion branching ratios is ±20%.

TABLE 3: Measured 298 K Reaction Rate Coefficients and Ion Product Branching Ratios for the Reactions of H_3O^+, CF_3^+, CF^+, CF_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, CO^+, N^+, N_2^+, Ar^+, F^+, and Ne^+ with TeF_6[a]

		TeF_6			
reagent ion	RE/eV	ion products	branching ratio (%)	reaction rate coefficient/10^{-9} cm^3 molecule^{-1} s^{-1}	
				present	Langevin
Ne^+	21.56	TeF_3^+	84	1.0	1.6
		TeF_4^+	4		
		TeF_5^+	12		
F^+	17.42	TeF_3^+	3	1.7	1.7
		TeF_5^+	97		
Ar^+	15.76	TeF_5^+	100	1.1	1.2
N_2^+	15.58	TeF_5^+	100	1.3	1.4
N^+	14.53	TeF_5^+	100	1.7	1.9
CO^+	14.01	FCO^+	55	1.3	1.4
		TeF_3^+	20		
		TeF_4^+	3		
		TeF_5^+	22		
CO_2^+	13.77	no reaction			1.2
O^+	13.62	TeF_5^+	100	1.8	1.8
N_2O^+	12.89	no reaction			1.2
H_2O^+	12.61	$(H_2OTeF_6)^+$			1.7
CF_2^+	11.42	CF_3^+	66	0.91	1.1
		TeF_3^+	10		
		TeF_4^+	6		
		TeF_5^+	18		
CF^+	9.11	no reaction			1.3
CF_3^+	≤8.9	no reaction			0.96
H_3O^+		no reaction			1.7

[a] The recombination energies (RE) in electronvolts (eV) of the reagent ions are listed. The Langevin (collisional) rate coefficients have been calculated (ref 13) and are shown for comparison with the experimental values. The estimated uncertainty in the measured rate coefficients and the product ion branching ratios is ±20%.

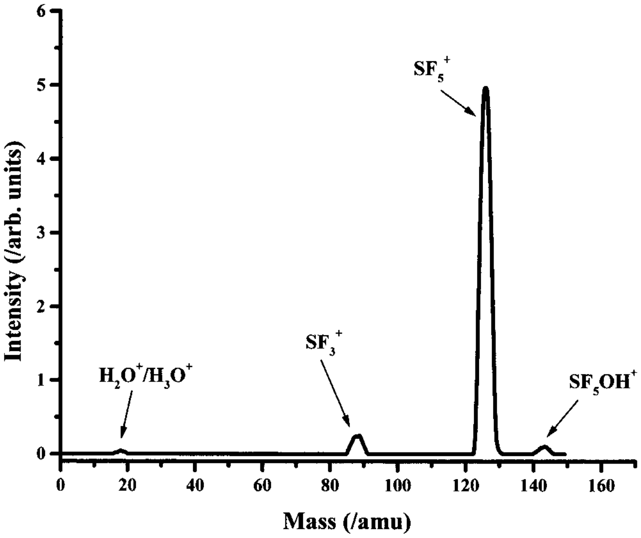

Figure 1. A typical mass spectrum obtained from the reaction of F^+ with SF_6. Two product ions are observed, SF_5^+ (dominant) and SF_3^+. The ion identified as SF_5OH^+ results from reactions of the impurity ion H_2O^+, formed in the flow tube from reaction of F^+ with trace H_2O, with SF_6. SF_5OH^+ must be the dominant ion in this reaction, although other product ions have been observed from the reaction of H_2O^+ with SF_6, for which no branching ratios are listed (ref 6).

unsaturated perfluorocarbons[23] show how the comparison of TPEPICO and flow-tube data can lead to a better fundamental understanding of the reactions. Photoionization studies are conducted at much lower pressures than flow-tube investigations of charge-transfer reactions. Differences can arise between product ion branching ratios from these two approaches when the unimolecular fragmentation of the initially formed parent ion is fast compared to the time scale of the experiment but slow compared to the rate of collisional stabilization. Evidence for this has been found in recent studies of charge-transfer reactions of benzene[24] and naphthalene.[25] Both of these molecules have stable, bound parent molecular ions, and the rate of fragmentation above the dissociation threshold is well described by statistical theories. In contrast, there is no evidence for the existence of stable XF_6^+ ions; once formed, these ions are expected to dissociate very rapidly over a repulsive potential energy surface. The product ion branching ratios for charge-transfer reactions of XF_6 are thus not expected to be sensitive to the buffer gas or the time scale of the experiment, and instead, differences compared to photoionization studies reflect the details of the dynamics of the encounter between XF_6 and the reagent ion.

3.1. SF_6 Reactions. The rate coefficients and product ion distributions for the reactions of H_3O^+, CF_3^+, CF^+, CF_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, CO^+, N^+, N_2^+, Ar^+, F^+, and Ne^+ with SF_6 are shown in Table 1. With the exception of the reactions of H_2O^+ and Ne^+, the dominant product ion is SF_5^+. This is illustrated in Figure 1 for the reaction of F^+ with SF_6, for which two ion products are observed, SF_3^+ (10%) and SF_5^+ (90%). The dissociative ionization limit to form SF_5^+ from SF_6 ($SF_6 \rightarrow SF_5^+ + F + e^-$) has been determined to be 14.0 ± 0.1 eV.[18] Therefore, all reagent ions with recombination energies greater than this value, that is, CO^+, N^+, N_2^+, Ar^+, F^+, and Ne^+, can energetically dissociatively charge-transfer to SF_6. However, the photoionization cross section for SF_6 is negligible at 14.0 eV. It is only at 15.33 eV that the photoionization cross section becomes significant, leading to an observed signal.[7,8] This means that for the reactions involving CO^+ and N^+, dissociative charge-transfer (if it occurs) can do so only by a short-range rather than a long-range mechanism.[4,6,12,23,26−30] A long-range mechanism requires energy resonance with nonzero Franck−Condon factors and no distortion of the potential energy curves, with all the available energy going into fragmentation. For a short-range charge-transfer, an intimate complex is formed within which chemical reaction pathways become available, that is, bonds may be broken and formed. In the case of the reactions with CO^+ and N^+, these chemical pathways would involve F^- abstraction from SF_6 to form the observed SF_5^+ product:

$$CO^+ + SF_6 \rightarrow SF_5^+ + FCO \qquad \Delta_r H° = -140 \text{ kJ mol}^{-1} \quad (4)$$

$$N^+ + SF_6 \rightarrow SF_5^+ + NF \qquad \Delta_r H° = -354 \text{ kJ mol}^{-1} \quad (5)$$

In agreement with the proposed short-range interaction, the minor product SF_3^+ (2%) observed for the reaction with N^+ requires an intimate interaction to make the overall reaction exothermic, involving the formation of either F_2 and NF (Williams et al.[6]) or NF_3:

$$N^+ + SF_6 \rightarrow SF_3^+ + F_2 + NF \qquad \Delta_r H° = -119 \text{ kJ mol}^{-1} \quad (6)$$

$$N^+ + SF_6 \rightarrow SF_3^+ + NF_3 \qquad \Delta_r H° = -500 \text{ kJ mol}^{-1} \quad (7)$$

We note that the dissociative charge-transfer channel leading to SF_3^+ is endothermic:

$$N^+ + SF_6 \rightarrow SF_3^+ + F_2 + F + N \qquad \Delta_r H° = +184 \text{ kJ mol}^{-1} \quad (8)$$

Reaction pathways 9 and 10 involving F abstraction, although exothermic, are not observed.

$$CO^+ + SF_6 \rightarrow FCO^+ + SF_5 \qquad \Delta_r H° = -184 \text{ kJ mol}^{-1} \quad (9)$$

$$N^+ + SF_6 \rightarrow NF^+ + SF_5 \qquad \Delta_r H° = -131 \text{ kJ mol}^{-1} \quad (10)$$

We note that the products of reactions 4 and 9 for the $CO^+ + SF_6$ reaction differ only in where the positive charge resides. The absence of reaction pathway 9 is surprising. Reaction 9 is more exothermic than reaction 4 because the ionization energy of FCO is less than that of SF_5, yet all the reactive flux goes through the less exothermic channel. For the $N^+ + SF_6$ reaction, the absence of the $NF^+ + SF_5$ exit channel is easier to explain on energetic grounds.

Of the four other reagent ions reported in this study which can exothermically charge-transfer with SF_6, the recombination energies of N_2^+ and Ar^+ are resonant with the $\tilde{X}$ ionic state of SF_6. From this and the high efficiency of the N_2^+ and Ar^+ reactions ($k_{exp}/k_c \approx 1$), Williams et al.[6] conclude that these two reactions occur via a long-range dissociative charge-transfer mechanism, resulting in the only observed ion product, SF_5^+:

$$N_2^+ + SF_6 \rightarrow SF_5^+ + F + N_2 \qquad \Delta_r H° = -151 \text{ kJ mol}^{-1} \quad (11)$$

$$Ar^+ + SF_6 \rightarrow SF_5^+ + F + Ar \qquad \Delta_r H° = -169 \text{ kJ mol}^{-1} \quad (12)$$

In agreement with this proposed mechanism, we note that only SF_5^+ is observed in the TPEPICO spectrum at photon energies corresponding to the recombination energies of N_2^+ and Ar^+.[7]

The recombination energy of F^+ (17.42 eV) lies on the high-energy shoulder of the $\tilde{A}/\tilde{B}$ photoelectron band of SF_6.[7,31] We may expect that when nonzero Franck−Condon factors are involved, a long-range (dissociative) charge-transfer may take place. However, this is not conclusive in itself because other factors, such as the type of molecular orbital from which the electron is ejected, can inhibit long-range charge-transfer.[23] In these circumstances, comparisons between TPEPICO and ion−molecule branching ratios are useful to decide if long-range charge-transfer is occurring. For the F^+ reaction, two product ions are observed, SF_5^+ (90%) and SF_3^+ (10%). By comparison, the TPEPICO data show that only SF_5^+ is produced at a photon energy of 17.42 eV. Thus, if dissociative charge-transfer does occur, the results suggest that it occurs via an intimate complex. Within such a complex, the formation of SF_5^+ (90%) and SF_3^+ (10%) can result from a short-range dissociative charge-transfer channel (reaction pathway 13) and/or through a chemical channel in which bonds are broken and formed (reaction pathway 14).

$$F^+ + SF_6 \rightarrow SF_5^+ + 2F \qquad \Delta_r H° = -329 \text{ kJ mol}^{-1} \quad (13a)$$

$$\rightarrow SF_3^+ + F_2 + 2F \qquad \Delta_r H° = -95 \text{ kJ mol}^{-1} \quad (13b)$$

$$F^+ + SF_6 \rightarrow SF_5^+ + F_2 \qquad \Delta_r H° = -488 \text{ kJ mol}^{-1} \quad (14a)$$

$$\rightarrow SF_3^+ + 2F_2 \qquad \Delta_r H° = -254 \text{ kJ mol}^{-1} \quad (14b)$$

There is no means of determining which reaction pathways dominate. A dissociative charge-transfer reaction pathway involving the reagent ion F^+ leading to SF_4^+ is exothermic, providing F_2 is eliminated from the transiently formed $(SF_6^+)^*$:

$$F^+ + SF_6 \rightarrow SF_4^+ + F_2 + F \qquad \Delta_r H° = -66 \text{ kJ mol}^{-1} \quad (15)$$

However, this product ion is not observed.

The reaction with Ne^+ is surprisingly efficient ($k_{exp}/k_c \approx 0.5$) given that the recombination energy of Ne^+ (21.56 eV) lies in a region of the SF_6 PES which is void of any structure, falling between the $\tilde{D}$ and $\tilde{E}$ ionic states of SF_6. This implies that a long-range charge-transfer mechanism is not operating. Instead, dissociative charge-transfer, leading to the three product ions (SF_3^+ (88%), SF_4^+ (2%), and SF_5^+ (10%)) as illustrated in Figure 2, must occur via a short-range interaction, for which Franck−Condon factors and energy resonances are unimportant:

$$Ne^+ + SF_6 \rightarrow SF_3^+ + F_2 + F + Ne \qquad \Delta_r H° = -495 \text{ kJ mol}^{-1} \quad (16a)$$

$$\rightarrow SF_3^+ + 3F + Ne \qquad \Delta_r H° = -336 \text{ kJ mol}^{-1} \quad (16b)$$

$$\rightarrow SF_4^+ + F_2 + Ne \qquad \Delta_r H° = -465 \text{ kJ mol}^{-1} \quad (16c)$$

$$\rightarrow SF_4^+ + 2F + Ne \qquad \Delta_r H° = -307 \text{ kJ mol}^{-1} \quad (16d)$$

$$\rightarrow SF_5^+ + F + Ne \qquad \Delta_r H° = -729 \text{ kJ mol}^{-1} \quad (16e)$$

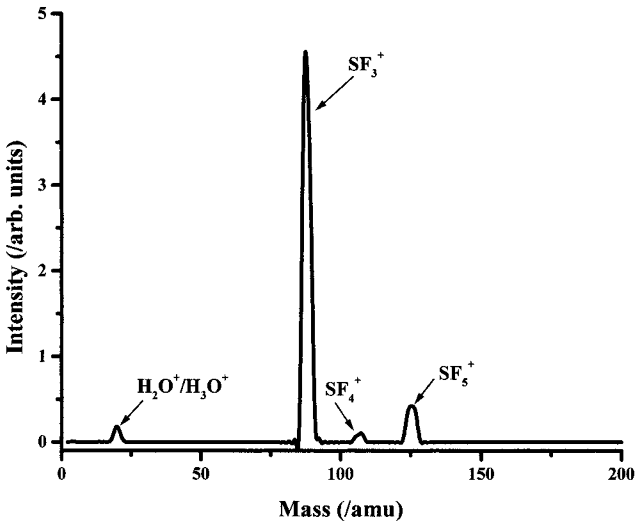

Figure 2. A typical mass spectrum obtained from the reaction of Ne^+ with SF_6, illustrating the greater degree of fragmentation as a result of the high recombination energy of Ne^+ (21.56 eV) compared to the other reagent ions used in this study. Three product ions are observed: SF_3^+ (dominant), SF_4^+, and SF_5^+.

Reactions of SF_6 with reagent ions whose recombination energies are <15.33 eV must proceed via an intimate ion–molecule complex in which bonds are broken and formed. With the exceptions of H_2O^+ and H_3O^+, the dominant product ion for all of these reactions is SF_5^+, formed by abstraction of F^- from SF_6 to the reagent ion within the complex:

$$M^+ + SF_6 \rightarrow SF_5^+ + MF \qquad (17)$$

$\Delta_r H° = -182, -120, -44$, and -47 kJ mol^{-1} for M = O, CF_2, CF, and CF_3, respectively. Ignoring entropic effects and knowing that $\Delta_r H°$ must be negative for a reaction to proceed at close to the Langevin rate, we note that the $CF^+ + SF_6 \rightarrow SF_5^+ + CF_2$ reaction shows that the value for the first dissociative ionization limit of $SF_6 \rightarrow SF_5^+ + F + e^-$ must be <14.45 eV. The reaction rate coefficients for M = CO_2 and N_2O are substantially below collisional. This is interpreted to be a result of a weak M–F bond, leading to these reactions being slightly endothermic.

The reaction of H_2O^+ with SF_6 has been reported by Williams et al.[6] and is clearly intimate in nature, requiring bond breaking and making; the product ions observed were OSF_4^+, $OHSF_5^+$, and $H_2OSF_6^+$, but we note that no branching ratios were reported by Williams et al. This is the first report of an ion reacting with SF_6 to give a product ion other than of the type SF_n^+. In this study, we have also observed one other reaction which did not result in a SF_n^+ product, namely, the reaction of CF^+ with SF_6 leading to the CF_3^+ product with a branching ratio of 5%:

$$CF^+ + SF_6 \rightarrow CF_3^+ + SF_4 \qquad \Delta_r H° = -291 \text{ kJ mol}^{-1} \qquad (18)$$

The corresponding F_2^- abstraction channel is endothermic

$$CF^+ + SF_6 \rightarrow SF_4^+ + CF_3 \qquad \Delta_r H° = +11 \text{ kJ mol}^{-1} \qquad (19)$$

and is not observed. For reactions involving the other ions with recombination energies <14.0 eV, in addition to the observed reaction pathway 17, other more exothermic reaction pathways are available. These include F-atom abstraction, for example, reaction pathways 9, 10, and 20, and F_2^- abstraction reactions, for example, reaction pathways 21 and 22.

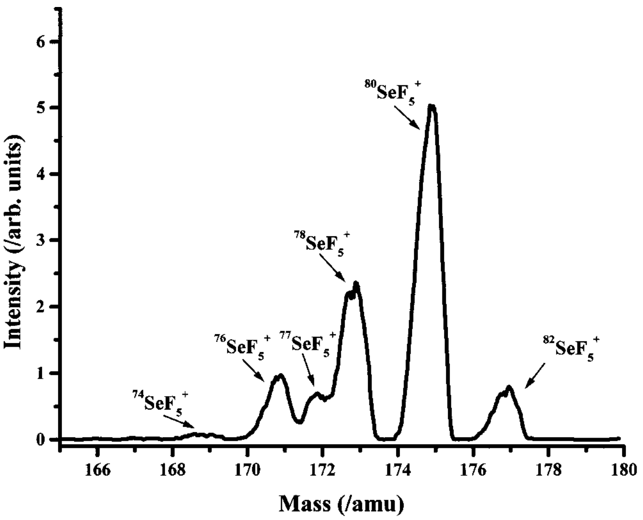

Figure 3. A high-resolution mass spectrum recording of the SeF_5^+ product ion (recorded here from the reaction of F^+ with SeF_6), identifying the selenium isotopes. The peak heights agree well with the relative abundance of these isotopes (ref 14).

$$CF_2^+ + SF_6 \rightarrow CF_3^+ + SF_5 \qquad \Delta_r H° = -224 \text{ kJ mol}^{-1} \qquad (20)$$

$$CO^+ + SF_6 \rightarrow SF_3^+ + F + CF_2O \qquad \Delta_r H° = -294 \text{ kJ mol}^{-1} \qquad (21a)$$

$$\rightarrow SF_4^+ + CF_2O \qquad \Delta_r H° = -265 \text{ kJ mol}^{-1} \qquad (21b)$$

$$CF_2^+ + SF_6 \rightarrow SF_3^+ + F + CF_4 \qquad \Delta_r H° = -269 \text{ kJ mol}^{-1} \qquad (22a)$$

$$\rightarrow SF_4^+ + CF_4 \qquad \Delta_r H° = -240 \text{ kJ mol}^{-1} \qquad (22b)$$

However, none of these channels are observed. As is commonly observed in ion–molecule reactions, this illustrates that exothermicity alone does not drive a reaction pathway, and other factors, such as potential energy barriers due to atomic rearrangements, may dominate the dynamics of an ion–molecule reaction.

H_3O^+ (the recombination energy of which corresponds to $H_3O^+ + e^- \rightarrow H_2O + H$) is unreactive with SF_6, in agreement with the two previous studies[3,6] and the thermochemistry. For example, the following reaction pathway is endothermic:

$$H_3O^+ + SF_6 \rightarrow SF_5^+ + HF + H_2O \qquad \Delta_r H° = +160 \text{ kJ mol}^{-1} \qquad (23)$$

3.2. SeF_6 Reactions. The reactions of the ions with SeF_6 are similar to those of SF_6, in that the majority result in SeF_5^+ being the dominant product ion (Table 2). Atomic selenium has more isotopes than sulfur. A high-resolution mass spectrum of the SeF_5^+ product ion is illustrated in Figure 3, which identifies the various isotopes in their correct abundance.[14] This unambiguously identifies the peak in the mass spectrum. Only forthe reactions of Ne^+, CO^+, CF_2^+, and CF_3^+ with SeF_6 is SeF_5^+ not the dominant product ion.

Using TPEPICO time-of-flight spectroscopy to determine the kinetic energy released in fragmentation over a range of energies, a value of 14.1 ± 0.5 eV for the first dissociative

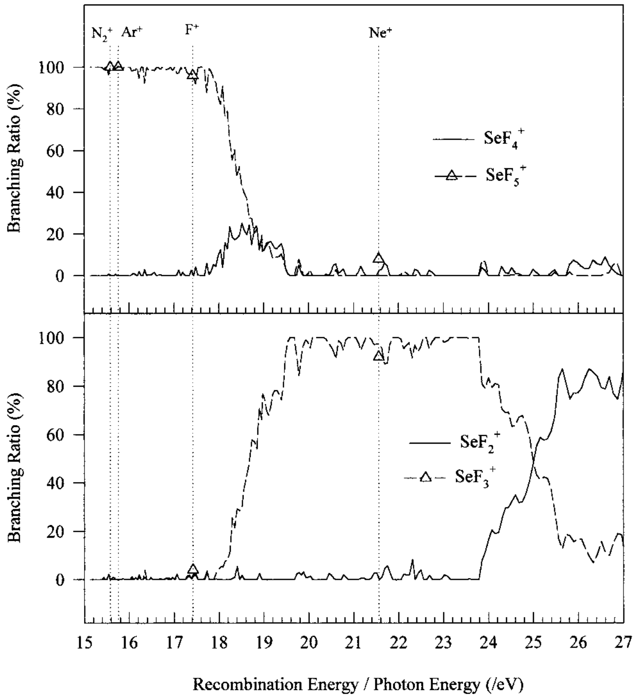

Figure 4. TPEPICO breakdown diagram for SeF_6 compared to the cation product branching ratios obtained from the reactions of N_2^+, Ar^+, F^+, and Ne^+ with SeF_6.

ionization energy ($SeF_6 \rightarrow SeF_5^+ + F + e^-$) has been determined.[8] However, the first onset of signal in the threshold photoelectron spectrum occurs at 15.3 eV. Thus, although all ions having recombination energies >14.1 eV can exothermically dissociatively charge-transfer with SeF_6, only those with recombination energies >15.3 eV are capable of doing so by a long-range mechanism. The recombination energies of N_2^+, Ar^+, F^+, and Ne^+ all lie in regions of the SeF_6 PES in which resonances are observed;[20,21] that is, nonzero Franck−Condon factors connect the ground electronic state of SeF_6 to its various ionic states at the recombination energies of these ions, a necessary condition for long-range charge-transfer to occur. The branching ratios obtained in the ion−molecule study are identical to those obtained in our TPEPICO measurements at the recombination energies of the N_2^+ and Ar^+ reagent ions.[8] At the recombination energies of F^+ and Ne^+, however, small differences in the branching ratios are observed (Figure 4). Although small, these differences are significant, that is, changes from zero in the TPEPICO results to a few percent in the ion−molecule results. Together with the observation that for these reactions $k_{exp} \approx k_c$, these observations imply a long-range dissociative charge-transfer mechanism for the reactions with N_2^+ and Ar^+ and an efficient short-range dissociative charge-transfer mechanism for the reactions with F^+ and Ne^+, leading to the observed product ions:

$$N_2^+ + SeF_6 \rightarrow SeF_5^+ + F + N_2 \quad \Delta_r H° = -143 \text{ kJ mol}^{-1} \tag{24}$$

$$Ar^+ + SeF_6 \rightarrow SeF_5^+ + F + Ar \quad \Delta_r H° = -160 \text{ kJ mol}^{-1} \tag{25}$$

$$F^+ + SeF_6 \rightarrow SeF_5^+ + 2F \quad \Delta_r H° = -321 \text{ kJ mol}^{-1} \tag{26a}$$

$$\rightarrow SeF_3^+ + F_2 + 2F \quad \Delta_r H° = -122 \text{ kJ mol}^{-1} \tag{26b}$$

$$\rightarrow SeF_3^+ + 4F \quad \Delta_r H° = +37 \pm 35 \text{ kJ mol}^{-1} \tag{26c}$$

$$Ne^+ + SeF_6 \rightarrow SeF_5^+ + F + Ne \quad \Delta_r H° = -720 \text{ kJ mol}^{-1} \tag{27a}$$

$$\rightarrow SeF_3^+ + F_2 + F + Ne \quad \Delta_r H° = -522 \text{ kJ mol}^{-1} \tag{27b}$$

$$\rightarrow SeF_3^+ + 3F + Ne \quad \Delta_r H° = -363 \text{ kJ mol}^{-1} \tag{27c}$$

That a short-range charge-transfer is suggested for reaction pathways 26 and 27 illustrates that energy resonance is a necessary but not sufficient criterion for long-range charge-transfer to occur. A recent study by us investigating charge-transfer from neutral perfluorocarbons to various cations suggests that the electron involved in an efficient long-range charge-transfer must be removed from a molecular orbital that is not shielded from the approaching reagent cation by other molecular orbitals of the reactant molecule.[23] It is possible that this is the case for molecular orbitals where electron removal results in the $\tilde{C}$ and $\tilde{E}$ ionic states of SeF_6 at 17.42 and 21.56 eV, respectively.

Because the uncertainty in the first dissociative ionization energy of $SeF_6 \rightarrow SeF_5^+ + F + e^-$ is as large as ± 0.5 eV, N^+, CO^+, CO_2^+, and O^+ reagent ions may also have enough energy to lead to charge-transfer with SeF_6, $(SeF_6^+)^* \rightarrow SeF_5^+ + F$. Given that the recombination energies of these reagent ions are significantly below the observed onset of ionization (15.3 eV), we suggest that if charge-transfer does occur, it will take place within an ion−molecule complex. Within such a complex, charge-transfer can compete with chemical reaction pathways in which new bonds are formed, leading not only to SeF_5^+ but to the other observed ion products. For the reactions of those ions whose recombination energies are less than the first dissociative ionization energy, N_2O^+, H_2O^+, CF_2^+, CF^+, and CF_3^+, the SeF_5^+ product ion must result from an intimate interaction in which a fluorine anion is abstracted from SeF_6 and forms a bond with the reagent ion, identical to reaction pathway 17 for SF_6:

$$M^+ + SeF_6 \rightarrow SeF_5^+ + MF \tag{28}$$

We note that $\Delta_r H° = -345, -131, -173, -111, -35 \pm 56$, and -38 ± 56 kJ mol^{-1} for M = N, CO, O, CF_2, CF, and CF_3, respectively. We also note that the rate coefficient for reaction 28 is significantly less than collisional for M = CO_2 and N_2O. As before, this probably indicates that the bond strengths of CO_2−F and N_2O−F are too weak to make the F^- abstraction exothermic or, in the case of the reaction with CO_2^+, that dissociative charge-transfer is slightly endothermic ($\Delta_r H° = +31$ kJ mol^{-1}). Similarly, the slow reaction with H_2O^+ implies that the reaction channel leading to SeF_5^+ is endothermic, in agreement with the thermochemistry; for example,

$$H_2O^+ + SeF_6 \rightarrow SeF_5^+ + OH + HF \quad \Delta_r H° = +71 \text{ kJ mol}^{-1} \tag{29}$$

In addition to SeF_5^+, other ion products are observed for the reactions of SeF_6 with CO^+, CF_2^+, and CF^+. For the reaction of CO^+, the dominant product ion is FCO^+ (52%), which results from neutral fluorine abstraction:

$$CO^+ + SeF_6 \rightarrow FCO^+ + SeF_5 \quad \Delta_r H° = \Delta_f H°(SeF_5) + 621 \text{ kJ mol}^{-1} \tag{30}$$

implying that $\Delta_fH°(SeF_5) < -621$ kJ mol^{-1}. This value is consistent with the bond dissociation energy, $D_0(SeF_5{-}F)$, of 3.15 eV,[32,33] from which a value for $\Delta_fH°(SeF_5)$ of -890 kJ mol^{-1} is obtained. Fluorine abstraction is also observed in the reaction of CF_2^+ with SeF_6, resulting in CF_3^+ being the dominant product ion with a branching ratio of 52%:

$$CF_2^+ + SeF_6 \rightarrow CF_3^+ + SeF_5 \qquad \Delta_rH° = \Delta_fH°(SeF_5) + 581 \text{ kJ mol}^{-1} \quad (31)$$

Surprisingly, the fluorine abstraction channel was not observed for the reactions of CO^+ and CF_2^+ with SF_6, although the reaction pathways 9 and 20 are extremely exothermic.

One other ion product observed from the reaction of CO^+ with SeF_6 is SeF_3^+ (14%), which results from F_2^- abstraction and F elimination:

$$CO^+ + SeF_6 \rightarrow SeF_3^+ + F + CF_2O \qquad \Delta_rH° = -321 \text{ kJ mol}^{-1} \quad (32)$$

The corresponding F^- abstraction and F_2 elimination channel is endothermic:

$$CO^+ + SeF_6 \rightarrow SeF_3^+ + FCO + F_2 \qquad \Delta_rH° = +67 \text{ kJ mol}^{-1} \quad (33)$$

The F_2^- abstraction channel leading to SeF_4^+, although exothermic, is not observed:

$$CO^+ + SeF_6 \rightarrow SeF_4^+ + CF_2O \qquad \Delta_rH° = -341 \text{ kJ mol}^{-1} \quad (34)$$

Energetically allowed pathways for the reaction of CF_2^+ with SeF_6 also involve F_2^- abstraction with (reaction pathway 35a) or without (reaction pathway 35b) fluorine elimination.

$$CF_2^+ + SeF_6 \rightarrow SeF_3^+ + F + CF_4 \qquad \Delta_rH° = -296 \text{ kJ mol}^{-1} \quad (35a)$$

$$\rightarrow SeF_4^+ + CF_4 \qquad \Delta_rH° = -316 \text{ kJ mol}^{-1} \quad (35b)$$

However, although these two reactions are highly exothermic, neither SeF_3^+ nor SeF_4^+ are observed ion products from the reaction of CF_2^+ with SeF_6.

F_2 abstraction occurs in the reaction of CF^+ with SeF_6 (as is also found for the reaction of CF^+ with SF_6, reaction pathway 18), leading to the observed CF_3^+ product ion:

$$CF^+ + SeF_6 \rightarrow CF_3^+ + SeF_4 \qquad \Delta_rH° = \Delta_fH°(SeF_4) + 369 \text{ kJ mol}^{-1} \quad (36)$$

We note that a much larger branching ratio is associated with the CF_3^+ ion for this reaction pathway, 74%, compared to the reaction with SF_6, 5%. The observation of CF_3^+ also suggests that $\Delta_fH°(SeF_4) < -369$ kJ mol^{-1}. Again, this value is consistent with the bond dissociation energy, $D_0(SeF_4{-}F)$ of 2.8 eV,[32,33] from which $\Delta_fH°(SeF_4) = -699$ kJ mol^{-1} is obtained.

H_3O^+ reacts with SeF_6, but it does so with a reaction rate coefficient significantly below the collisional value. We were unable to unambiguously determine the product ion, being unwilling to use a limited SeF_6 sample for a slow reaction. Therefore, we cannot guarantee that H_3O^+ was not reacting efficiently with some unknown impurity in the SeF_6 sample. Thus, the rate coefficient obtained, 1×10^{-12} cm^3 s^{-1}, represents an upper limit.

3.3. TeF_6 Reactions. Compared to SF_6 and SeF_6, fewer of the reagent ions react with TeF_6, but those that do generally show a richer ion chemistry than that observed for the corresponding reactions with SF_6 and SeF_6, as is illustrated in Table 3. For ions whose recombination energies are >14.5 eV, the dominant product ion (with the exception of the Ne^+ reaction) is TeF_5^+. Our recent TPEPICO study indicates that the dissociative ionization limit of TeF_6, leading to $TeF_5^+ + F + e^-$, occurs at 14.5 ± 0.6 eV.[8] However, the cross section for photodissociative ionization at this energy is zero; the onset of signal in the TPES occurs at 15.4 ± 0.2 eV. Therefore, dissociative charge-transfer from N^+, reaction pathway 37, is unlikely to take place by a long-range mechanism, which as mentioned previously requires energy resonance with non-zero Franck−Condon factors. It seems more likely that dissociative charge-transfer takes place via an ion−molecule complex in which competition with a chemical pathway, reaction pathway 38, might occur, leading to the observed TeF_5^+ product ion.

$$N^+ + TeF_6 \rightarrow TeF_5^+ + F + N \qquad \Delta_rH° = -3 \pm 65 \text{ kJ mol}^{-1} \quad (37)$$

$$N^+ + TeF_6 \rightarrow TeF_5^+ + NF \qquad \Delta_rH° = -306 \text{ kJ mol}^{-1} \quad (38)$$

It is not usually possible to determine whether dissociative charge-transfer has occurred or not, because no information on the neutral product(s) is obtained in the SIFT experiments.

The recombination energies of N_2^+ and Ar^+ lie in regions of the TeF_6 PES and TPES in which resonances are observed.[20,8] Furthermore, the reactions of TeF_6 with these two ions occur with unit efficiencies ($k_{exp} = k_c$). Therefore, long-range dissociative charge-transfer is the proposed mechanism leading to the observed ion products:

$$N_2^+ + TeF_6 \rightarrow TeF_5^+ + F + N_2 \qquad \Delta_rH° = -104 \text{ kJ mol}^{-1} \quad (39)$$

$$Ar^+ + TeF_6 \rightarrow TeF_5^+ + F + Ar \qquad \Delta_rH° = -121 \text{ kJ mol}^{-1} \quad (40)$$

The recombination energy of F^+ also lies in a region of the PES and TPES of TeF_6 in which signal is observed. Therefore, long-range dissociative charge-transfer is suggested given that the reaction occurs with unit efficiency. However- ,although dissociative charge-transfer can explain the TeF_5^+ product ion,

$$F^+ + TeF_6 \rightarrow TeF_5^+ + 2F \qquad \Delta_rH° = -282 \text{ kJ mol}^{-1} \quad (41a)$$

this mechanism cannot produce the minor TeF_3^+ product ion:

$$F^+ + TeF_6 \rightarrow TeF_3^+ + F_2 + 2F \qquad \Delta_rH° = +90 \text{ kJ mol}^{-1} \quad (41b)$$

TeF_3^+ can occur only via an intimate reaction in which F^- is transferred to the F^+ reagent ion:

$$F^+ + TeF_6 \rightarrow TeF_3^+ + 2F_2 \qquad \Delta_r H° = -69 \text{ kJ mol}^{-1} \tag{41c}$$

Ne^+ reacts with TeF_6 via dissociative charge-transfer, resulting in more product ions than are observed for the other reagent ions which are energetically capable of dissociative charge-transfer to TeF_6. The observed ion products are TeF_3^+ (84%), TeF_4^+ (4%), and TeF_5^+ (12%):

$$Ne^+ + TeF_6 \rightarrow TeF_5^+ + F + Ne \qquad \Delta_r H° = -682 \text{ kJ mol}^{-1} \tag{42a}$$

$$\rightarrow TeF_4^+ + 2F + Ne \qquad \Delta_r H° = -180 \text{ kJ mol}^{-1} \tag{42b}$$

$$\rightarrow TeF_4^+ + F_2 + Ne \qquad \Delta_r H° = -339 \text{ kJ mol}^{-1} \tag{42c}$$

$$\rightarrow TeF_3^+ + F_2 + F + Ne \qquad \Delta_r H° = -310 \text{ kJ mol}^{-1} \tag{42d}$$

$$\rightarrow TeF_3^+ + 3F + Ne \qquad \Delta_r H° = -151 \text{ kJ mol}^{-1} \tag{42e}$$

The recombination energy of Ne^+ lies in a structureless region of the PES and TPES of TeF_6, between the $\tilde{E}$ and $\tilde{F}$ ionic states.[20,8] Thus, there are no energy resonances connecting TeF_6 to an ionic state at this energy, and therefore long-range charge-transfer must be inhibited. Although the reaction efficiency is less than unity ($k_{exp}/k_c \approx 0.63$), k_{exp} is still a significant fraction of the collisional value. We therefore assume that a reasonably efficient short-range dissociative charge-transfer mechanism is occurring.

In confirmation of the proposed long-range (reactions with N_2^+ and Ar^+) and short-range (reactions with F^+ and Ne^+) charge-transfer mechanisms, the TPEPICO branching ratios of TeF_6 at the various reagent ion recombination energies are identical to those obtained in the ion−molecule reactions with N_2^+ and Ar^{+8} and slightly but significantly different from those obtained in the reactions with F^+ and Ne^+ (Figure 5). At the recombination energies of F^+ and Ne^+, only one product ion is observed in the TPEPICO spectra, TeF_5^+ (at 17.4 eV) and TeF_3^+ (at 21.6 eV). Such differences in the ion branching ratios may imply that a short-range charge-transfer pathway (an intimate pathway) has taken place for that reaction.[6,23]

For the other reagent ions (H_3O^+, CF_3^+, CF^+, CF_2^+, H_2O^+, N_2O^+, O^+, CO_2^+, and CO^+), charge-transfer is energetically impossible. These ions may then react with TeF_6 only via a complex, within which bonds may be broken and formed leading to products such as those obtained in reaction pathway 38. Of these ions, only CO^+, O^+, and CF_2^+ are found to react efficiently with TeF_6, with k_{exp} being close to the calculated collisional value.

For the O^+ reaction, only one product ion is observed, TeF_5^+, resulting from F^- abstraction from TeF_6:

$$O^+ + TeF_6 \rightarrow TeF_5^+ + FO \qquad \Delta_r H° = -135 \text{ kJ mol}^{-1} \tag{43}$$

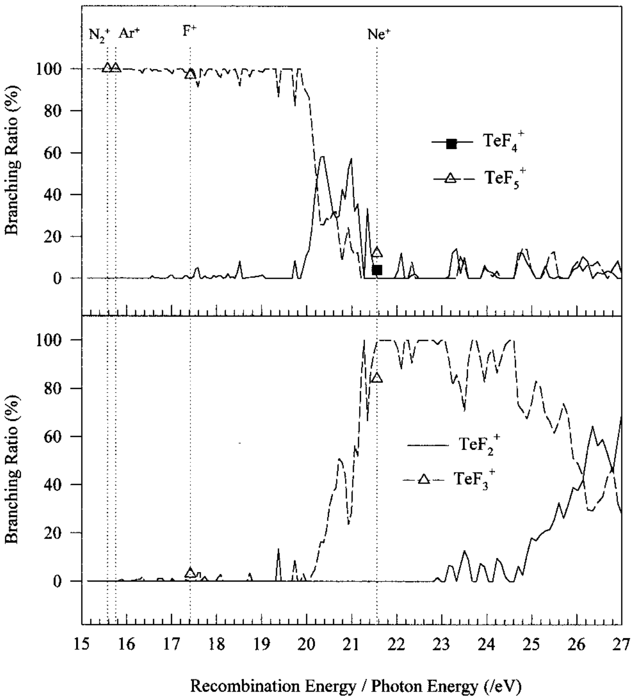

Figure 5. TPEPICO breakdown diagram for TeF_6 compared to the cation product branching ratios obtained from the reactions of N_2^+, Ar^+, F^+, and Ne^+ with TeF_6.

The reactions of CO^+ and CF_2^+ with TeF_6 result in four product ions, the dominant ion being MF^+ from F abstraction:

$$CO^+ + TeF_6 \rightarrow FCO^+ + TeF_5 \qquad \Delta_r H° = \Delta_f H°(TeF_5) + 822 \text{ kJ mol}^{-1} \tag{44}$$

$$CF_2^+ + TeF_6 \rightarrow CF_3^+ + TeF_5 \qquad \Delta_r H° = \Delta_f H°(TeF_5) + 782 \text{ kJ mol}^{-1} \tag{45}$$

That reaction pathway 44 is observed indicates that $\Delta_f H°(TeF_5) < -822$ kJ mol^{-1}. The other ion products resulting from the reactions of CO^+ and CF_2^+ with TeF_6 are the same, namely, TeF_3^+, TeF_4^+, and TeF_5^+, and these are formed with similar branching ratios (see Table 3). The only exothermic route available for the production of TeF_3^+ and TeF_4^+ is via F_2^- abstraction to the CO^+ or CF_2^+ reagent ion:

$$CO^+ + TeF_6 \rightarrow TeF_3^+ + F + CF_2O \qquad \Delta_r H° = -109 \text{ kJ mol}^{-1} \tag{46a}$$

$$\rightarrow TeF_4^+ + CF_2O \qquad \Delta_r H° = -138 \text{ kJ mol}^{-1} \tag{46b}$$

$$CF_2^+ + TeF_6 \rightarrow TeF_3^+ + F + CF_4 \qquad \Delta_r H° = -84 \text{ kJ mol}^{-1} \tag{47a}$$

$$\rightarrow TeF_4^+ + CF_4 \qquad \Delta_r H° = -113 \text{ kJ mol}^{-1} \tag{47b}$$

The F^- abstraction pathways, with the elimination of F_2 (reaction pathways 48a and 49a) or the elimination of F (reaction pathways 48b and 49b) leading to the product ions TeF_3^+ and TeF_4^+, respectively, are highly endothermic and therefore cannot occur.

Although the F_2^- abstraction pathways are also energetically allowed for the reactions of CO^+ and CF_2^+ with SF_6 (reaction

$$CO^+ + TeF_6 \rightarrow TeF_3^+ + F_2 + FCO \qquad \Delta_r H° = +279 \text{ kJ mol}^{-1} \quad (48a)$$

$$\rightarrow TeF_4^+ + F + FCO \qquad \Delta_r H° = +409 \text{ kJ mol}^{-1} \quad (48b)$$

$$CF_2^+ + TeF_6 \rightarrow TeF_3^+ + F_2 + CF_3 \qquad \Delta_r H° = +299 \text{ kJ mol}^{-1} \quad (49a)$$

$$\rightarrow TeF_4^+ + F + CF_3 \qquad \Delta_r H° = +429 \text{ kJ mol}^{-1} \quad (49b)$$

pathways 21 and 22) and with SeF_6 (reaction pathways 32, 34, and 35), they also are not observed.

The TeF_5^+ product ion resulting from the reactions of CO^+ and CF_2^+ with TeF_6 occurs by F^- abstraction from TeF_6 to these reagent ions in an ion−molecule complex:

$$CO^+ + TeF_6 \rightarrow TeF_5^+ + FCO \qquad \Delta_r H° = -93 \text{ kJ mol}^{-1} \quad (50)$$

$$CF_2^+ + TeF_6 \rightarrow TeF_5^+ + CF_3 \qquad \Delta_r H° = -72 \text{ kJ mol}^{-1} \quad (51)$$

That the reagent ions CO_2^+ and N_2O^+ show no reaction with TeF_6 suggests that the F^- abstraction channel is endothermic (again presumably because the CO_2−F and N_2O−F bond strengths are too weak to drive the reaction). The absence of reaction of CF^+ and CF_3^+ with TeF_6 may imply that the pathways observed in the reactions of the ions with SF_6 and SeF_6, namely, F_2 (reaction pathway 52a) and F^- abstraction (reaction pathways 52b and 53), are not energetically available.

$$CF^+ + TeF_6 \rightarrow CF_3^+ + TeF_4 \qquad \Delta_r H° = \Delta_f H°(TeF_4) + 570 \text{ kJ mol}^{-1} \quad (52a)$$

$$\rightarrow TeF_5^+ + CF_2 \qquad \Delta_r H° = +4 \pm 65 \text{ kJ mol}^{-1} \quad (52b)$$

$$CF_3^+ + TeF_6 \rightarrow TeF_5^+ + CF_4 \qquad \Delta_r H° = +1 \pm 65 \text{ kJ mol}^{-1} \quad (53)$$

The lack of observation of reaction pathway 52a may imply that $\Delta_f H°(TeF_4) > -570$ kJ mol^{-1}. However, care must be taken in assigning heats of formation through unobserved ion−molecule channels. We have already observed that not all exothermic pathways may be followed, possibly because of a potential energy barrier inhibiting the efficiency of that pathway.

For the H_2O^+ and H_3O^+ reagent ions, no bimolecular reactions with TeF_6 were observed. This is because any obvious reaction pathways are endothermic; for example,

$$H_2O^+ + TeF_6 \rightarrow TeF_5^+ + OH + HF \qquad \Delta_r H° = +110 \text{ kJ mol}^{-1} \quad (54)$$

$$H_3O^+ + TeF_6 \rightarrow TeF_5^+ + H_2O + HF \qquad \Delta_r H° = +207 \text{ kJ mol}^{-1} \quad (55)$$

An association product ion was observed with the reaction of H_2O^+, $(H_2OTeF_6)^+$, for which no termolecular rate coefficient was determined because of the need to conserve the TeF_6 sample.

4. Concluding Remarks

The first study of the gas-phase reactions of ions with SeF_6 and TeF_6 has been presented in this paper. Rate coefficients and product ion distributions are reported for the reactions of 14 atomic and molecular reagent cations. These reactions have been compared with those of SF_6, providing a better understanding of the cation chemistry of SF_6, an important additive in reactive plasmas. A wide variety of reaction processes are evident, including dissociative charge-transfer and notably various abstraction routes. Although there are many similarities in the reaction rate coefficients and product ion branching ratios for the reactions of the various reagent ions with SF_6, SeF_6, and TeF_6, there are noticeable differences. Vacuum ultraviolet photoelectron and threshold photoelectron−photoion coincidence spectra have been used to help interpret the results. For the reagent ions whose recombination energies are greater than the ionization potentials of the neutral group 6B molecules, rate coefficients and branching ratios are governed by the accessibility of ionic states. If there is no resonance feature in the PES of the neutral molecule, then (dissociative) charge-transfer reactions proceed via a short-range mechanism. Differences in the ion branching ratios between those obtained in this ion−molecule study and those obtained from the TPEPICO measurements, at the recombination energy of the reagent ion, may then be apparent. We suggest that for those reagent ions whose recombination energies are greater than the lowest dissociative ionization limit of the reactant molecule ($XF_6 \rightarrow XF_5^+ + F + e^-$) but less than the observed onset of ionization, dissociative charge-transfer can take place only via an intimate encounter. Within the ion−molecule complex formed, other (chemical) reaction channels, in which bonds are broken and formed, may compete with the dissociative charge-transfer channel. For reagent ions whose recombination energies are less than the lowest dissociative ionization limit of the reactant molecule, only chemical reaction pathways are energetically favorable. Notably, F^-, F, F_2^-, and F_2 abstraction pathways have been observed.

This study represents only an initial investigation of the ion chemistry of SeF_6 and TeF_6. We are extending this study, investigating other ion reactions including cations and anions. Recently, we have studied the reactions of O_2^-, O^-, OH^-, F^-, and CF_3^- with SF_6, SeF_6, and TeF_6, the results of which will be the subject of a forthcoming paper.

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References and Notes

(1) Fehsenfeld, F. C. *J. Chem. Phys.* **1971**, *54*, 438.
(2) Bowers, M. T.; Chau, M. *J. Phys. Chem.* **1976**, *80*, 1739.
(3) Babcock, L. M.; Streit, G. E. *J. Chem. Phys.* **1981**, *74*, 5700.
(4) Shul, R. J.; Upschulte, B. L.; Passarella, R.; Keesee, R. G.; Castlemann, A. W., Jr. *J. Phys. Chem.* **1987**, *91*, 2556.
(5) Morris, R. A.; Miller, T. M.; Viggiano, A. A.; Paulson, J. F. *J. Geophys. Res.* **1995**, *100*, 12.
(6) Williams, T. L.; Babcock, L. M.; Adams, N. G. *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 759.
(7) Creasey, J. C.; Jones, H. M.; Smith, D. M.; Tuckett, R. P.; Hatherly, P. A.; Codling, K. *Chem. Phys.* **1993**, *174*, 331.
(8) Jarvis, G. K.; Mayhew, C. A.; Chim, R. Y. L.; Kennedy, R. A.; Tuckett, R. P. *Chem. Phys. Lett.* **2000**, *320*, 104.
(9) Adams, N. G.; Smith, D. In *Techniques for the Study of Ion-Molecule Reactions*; Farrar, J. M., Saunders, W. H., Eds.; Wiley: New York, 1988; p 165.
(10) Smith, D.; Adams, N. G. *Adv. At. Mol. Phys.* **1988**, *24*, 1.
(11) Smith, D.; Adams, N. G. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *21*, 349.
(12) Jarvis, G. K.; Mayhew, C. A.; Tuckett, R. P. *J. Phys. Chem.* **1996**, *100*, 17166.

(13) Gioumousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1959**, *29*, 294.

(14) *CRC Handbook of Chemistry and Physics*, 80th ed.; Lide, D. R., Ed.; CRC Press Inc.: Boca Raton, FL, 1999.

(15) Irikura, K. K. *J. Am. Chem. Soc.* **1999**, *121*, 7689.

(16) NIST Chemistry WebBook, NIST Standard Reference Database Number 69. http://webbook.nist.gov (accessed Feb 2000). Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD.

(17) Fisher, E. R.; Kickel, B. L.; Armentrout, P. B. *J. Chem. Phys.* **1992**, *97*, 4859.

(18) Tichy, M.; Javahery, G.; Twiddy, N. D.; Fergusson, E. E. *Int. J. Mass Spectrom. Ion Phys*. **1987**, *79*, 231.

(19) Jarvis, G. K.; Tuckett, R. P. *Chem. Phys. Lett.* **1998**, *295*, 145.

(20) Potts, A. W.; Lempka, H. J.; Streets, D. G.; Price, W. C. *Philos. Trans. R. Soc. London* **1970**, *A268*, 59.

(21) Addison, B. M.; Tan, K. H.; Bancroft, G. M.; Cerrina, F. *Chem. Phys. Lett.* **1986**, *129*, 468.

(22) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl.* **1988**, *1*, 17.

(23) Jarvis, G. K.; Kennedy, R. A.; Mayhew, C. A.; Tuckett, R. P. *Int. J. Mass Spectrom*. **2000**, *202*, 323.

(24) Arnold, S. T.; Williams, S.; Dotan, I.; Midey, A. J.; Morris, R. A.; Viggiano, A. A. *J. Phys. Chem. A* **1999**, *103*, 8421.

(25) Midey, A. J.; Williams, S.; Arnold, S. T.; Dotan, I.; Morris, R. A.; Viggiano, A. A. *Int. J. Mass Spectrom.* **2000**, *195*, 327.

(26) Bowers, M. T.; Elleman, D. D. *Chem. Phys. Lett.* **1972**, *16*, 486.

(27) Gauglhofer, J.; Kevan, W. T., Jr. *Chem. Phys. Lett.* **1972**, *16*, 492.

(28) Laudenslager, J. B.; Huntress, W. T., Jr.; Bowers, M. T. *J. Chem. Phys.* **1974**, *61*, 4600.

(29) Shul, R. J.; Upsculte, B. L.; Keesee, R. G.; Castleman, A. W., Jr. *J. Chem. Phys.* **1987**, *86*, 4446.

(30) Mayhew, C. A. *J. Phys. B*: *At. Mol. Opt. Phys.* **1992**, *25*, 1865.

(31) Bieri, G.; Asbrink, L.; von Niessen, W. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *26*, 173.

(32) Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1978**, *68*, 2023.

(33) Li, Q.; Xu, W.; Xie, Y.; Schaefer, H. F. *J. Phys. Chem. A* **1999**, *103*, 7496.