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Gas-Phase Reactions of Sulfur Hexafluoride with Transition Metal and Main Group Atomic Cations: Room-Temperature Kinetics and Periodicities in Reactivity

Ping Cheng,[†] Alireza Shayesteh, and Diethard K. Bohme*

Department of Chemistry, Centre for Research in Mass Spectrometry and Centre for Research in Earth and Space Science, York University, Toronto, Ontario M3J 1P3, Canada

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Gas-phase reactions of SF_6 were investigated with 46 different atomic metal and main group cations at room temperature using an Inductively-Coupled Plasma/Selected-Ion Flow Tube (ICP/SIFT) tandem mass spectrometer. The atomic ions were produced at about 5500 K in the ICP source and allowed to decay radiatively and to thermalize by collisions with argon and helium atoms prior to reaction downstream in a flow tube in helium buffer gas at 0.35 ± 0.01 Torr and 295 ± 2 K. Rate coefficients and product distributions were measured for the reactions of fourth-row atomic ions from K^+ to Se^+, of fifth-row atomic ions from Rb^+ to Te^+ (excluding Tc^+), and of sixth-row atomic ions from Cs^+ to Bi^+. The early transition metal ions react with SF_6 very efficiently ($k/k_c = 0.56-0.96$) to produce MF_m^+ ($m = 1-4$) and SF_n^+ ($n = 1-4$) ions, whereas the late transition metal ions react much less efficiently ($k/k_c < 0.2$) to form $M^+(SF_6)$ adduct ions. Reactions of SF_6 with Ca^+, Sr^+, Ba^+, Ge^+, and As^+ proceed efficiently ($k/k_c = 0.35-0.85$) through various channels, while all other main group metal ions are inert toward sulfur hexafluoride. Primary and seconday adduct formation was observed to exhibit equilibrium kinetics, and the standard free energy change for SF_6 addition is found to correlate with the efficiency of addition according to $\log[k/k_c] = -8.7 + 7.8 \log[-\Delta G°/(\text{kcal mol}^{-1})]$. Several MF_m^+ ions were observed to react further with SF_6 to produce MF_{m+k}^+, SF_n^+, and $MF_m^+(SF_6)$ as secondary products.

1. Introduction

The chemical and physical properties of sulfur hexafluoride have been of considerable interest for several decades. With its octahedrally coordinated sulfur center effectively shielded by the six fluorine atoms, SF_6 expresses chemical inertness and has a relatively high dielectric constant. Because of these properties, SF_6 is widely used in industry as a gaseous insulator in high-power electrostatic generators, transformers, condensers and cables.[1] SF_6 also has been used as a source of fluorine atoms in plasma etching technology.[2] Furthermore, sulfur hexafluoride serves as an excellent example for hypervalent compounds generally.[3,4] Extensive research with a variety of experimental techniques has been directed toward studies of the bonding in SF_6 and the ionization of this molecule.[5−12] The molecular ion SF_6^+ has been found to be unstable relative to dissociation into SF_5^+ and F.[11,12]

The first experimental study on gas-phase reactions of SF_6 with atomic and molecular ions was reported in 1971 by Fehsenfeld[13] and several other ion−molecule reactions of

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* To whom correspondence should be addressed. E-mail: dkbohme@yorku.ca. Phone: 416-736-2100, ext 66188. Fax: 416-736-5936.

[†] Present address: Elemento-Organic Chemistry Laboratory, Nankai University, Tianjin 300071, China.

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SF_6 have been investigated since then.[14−24] Jiao and Freiser[25] performed the first systematic investigation of the reactions of 21 transition-metal monocations with SF_6 using FT-ICR mass spectrometry, with particular attention given to the Sc^+ ion. The results of these reactivity measurements led these authors to propose that at least one empty valence d orbital of the metal ion with proper symmetry is needed for reaction to occur. Gibson and co-workers[26,27] have recently reported gas-phase reactions of bare and ligated uranium and protactinium ions with SF_6.

Instrumental developments in our laboratory have provided the means to survey trends in chemical kinetics for reactions of atomic monocations with neutral molecules across and down most of the periodic table. For example, we have surveyed previously reactions of more than 50 bare atomic cations, including lanthanide cations, with O_2,[28,29] NO,[30,31] D_2O,[32,33] CO_2,[34,35] N_2O,[36,29] CS_2,[37,35] CH_3F,[38,39] CH_3Cl,[40] benzene[41] and hexafluorobenzene[42,43] molecules. Quite recently we reported experimental results for gas-phase reactions of the lanthanide ions with SF_6.[44] Here we explore the kinetics of reactions of the fourth-, fifth- and sixth-row atomic ions with SF_6 with a focus on trends in reaction efficiency and product formation. The atomic ions (M^+) were all generated in an Inductively-Coupled Plasma (ICP) source, and were allowed to react with SF_6 at room temperature in helium buffer gas at 0.35 ± 0.01 Torr using a Selected-Ion Flow Tube (SIFT) tandem mass spectrometer.

2. Experimental Section

The experimental results reported here were obtained using the Selected-Ion Flow Tube (SIFT) tandem mass spectrometer described in detail elsewhere.[45,46] This instrument was recently modified to accept ions generated in an inductively coupled plasma (ICP) torch (ELAN series, Perkin-Elmer SCIEX) through an atmosphere/vacuum interface. The ICP ion source and interface have also been described previously.[47,48] Solutions containing the metal salt of interest with concentrations of about 5 μg L^{-1} were peristaltically pumped via a nebulizer into the plasma. The nebulizer flow was adjusted to maximize the ion signal detected downstream of the flow tube. The sample solutions were prepared using atomic spectroscopy standard solutions commercially available from SPEX, Teknolab, J.T. Baker Chemical Co., Fisher Scientific Company, Perkin-Elmer, and Alfa Products. Aliquots of standard solutions were diluted with highly purified water produced in the Millipore Milli-Qplus ultrapure water system. Single-isotope solutions were used for $M^+(m/z) = Ca^+(44)$ and $Se^+(80)$. Readily soluble compounds of these metals were obtained from Oak Ridge National Laboratory. The final concentrations were varied between 5 and 20 ppm to achieve a suitable intensity of the resultant ion beam. A stabilizing agent was usually added to each solution to prevent precipitation: KOH for base-stabilized slats, HNO_3 or HCl for acid-stabilized salts.

Atomic ions emerge from the ICP at a nominal ion temperature of 5500 K with the corresponding Boltzmann distributions. The electronic state populations at this temperature have been calculated previously[36] from available optical spectra.[49,50] These calculations show that excited states of the main group elemental cations except Ba^+ contribute very little (never more than 10%) to the total ion population at 5500 K; the ground ^2S state and the excited ^2D state of Ba^+ contribute 44% and 55%, respectively. The electronic-state distributions at 5500 K are more variable for the transition metal cations: excited states contribute less than 20% to the populations of Cr^+, Mn^+, Ni^+, Cu^+, Zn^+, Rh^+, Pd^+, Ag^+, Cd^+, Re^+, Au^+, and Hg^+, 20−50% to the populations of Sc^+, V^+, Fe^+, Co^+, Mo^+, Ru^+, Hf^+, Ta^+, W^+, and Pt^+, and more than 50% for Ti^+, Y^+, Zr^+, Nb^+, La^+, and Ir^+ ions. After extraction from the ICP, the plasma ions may experience electronic-state relaxations via both radiative decay and collisional energy transfer. The latter may occur by collisions

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with argon, as the extracted plasma cools upon sampling, and with helium in the flow tube (ca. 4 × 10^5 collisions with helium) prior to the reaction region. Almost all of the low-lying electronic states of these transition-metal ions have even parity; electric dipole transitions between states of the same parity are forbidden (Laporte rule).[51] This means that radiative decays of the excited electronic states in these cations can occur only by magnetic dipole or electric quadrupole transitions. The probabilities for these transitions are very low,[52] and the resulting radiative lifetimes are of the order of seconds or larger. In the ICP/SIFT experiments, the time interval between the exit of the ICP source and the entrance of the reaction region is about 20 msec, and therefore no major modification of state distributions can occur in this time interval via forbidden radiative decay. That having been said, there were no indications of excited-state effects in our previous measurements of reactions of atomic cations derived from the same ICP source with N_2O, except for Pt^+.[36] The many collisions experienced by the atomic cations with the quite polarizable argon atoms as they emerge from the ICP and the about 4 × 10^5 collisions with helium atoms in the flow tube (the helium buffer gas pressure was 0.35 ± 0.01 Torr) appear to be sufficient to thermalize the excited states and to ensure that the atomic ions reach a translational temperature equal to the tube temperature of 295 ± 2 K prior to entering the reaction region. However, the exact extent of electronic relaxation is uncertain. Clues to the presence of excited electronic states of the atomic ions in the reaction region can be found in the product ions observed and in the shape of the semilogarithmic decay of the reacting atomic ion upon addition of neutral reactants. Curvature will appear in the measured atomic-ion decay when the ground state and excited state react at different rates even when they give the same product ions. An excited-state effect cannot be seen when the products and reaction rates are the same for both the ground and excited states, but in this case the measured atomic-ion decay defines the ground-state kinetics. Our growing experience has shown that excited states can reveal themselves when the ground state of the atomic ion reacts only slowly by termolecular addition and excited states react rapidly in a bimolecular fashion.

Reactions of 46 atomic ions, fourth-row cations from K^+ to Se^+, fifth-row cations from Rb^+ to Te^+ (excluding Tc^+), and sixth-row cations from Cs^+ to Bi^+, were investigated with SF_6 at a helium buffer gas pressure of 0.35 ± 0.01 Torr and temperature of 295 ± 2 K. The highly pure SF_6 gas was obtained commercially (BOC, >99.9%) and introduced into the reaction region of the SIFT as a dilute (15%) mixture in helium (Air Liquide, 99.997%). Reaction rate coefficients were determined in the usual manner using pseudo first-order kinetics,[45,46] and the rate coefficients for the primary and consecutive reactions reported herein have an estimated absolute accuracy of ± 30%.[53]

3. Results and Discussion

The primary reactions exhibit a wide range of reactivity with the measured rate coefficients ranging from $<10^{-13}$ (K^+) to 9.6 × 10^{-10} (Ti^+) cm^3 $molecule^{-1}$ s^{-1}. The following four reaction channels were observed (here the nature of the neutral product in reactions 1a and 1b, not observed experimentally, is uncertain and may involve further dissociation):

$$M^+ + SF_6 \rightarrow MF_m^+ + SF_{6-m} \qquad m = 1-3 \qquad (1a)$$

$$\rightarrow SF_n^+ + MF_{6-n} \qquad n = 1-5 \qquad (1b)$$

$$\rightarrow MSF_5^+ + F \qquad (1c)$$

$$\rightarrow M^+(SF_6) \qquad (1d)$$

The observed reactions include what formally can be described as single or multiple F atom transfer, reaction 1a; single or multiple F atom transfer accompanied by electron transfer upon product separation, reaction 1b; addition accompanied by F atom elimination, reaction 1c, and SF_6 addition, reaction 1d. As expected from the available ionization energies (IE) of metal ions, which are far below that of SF_6 (IE = 15.7 eV),[54] electron transfer was not observed for any of the metal ions studied here.

Of the 46 atomic ions investigated, 16 ions reacted efficiently with SF_6 through one or more of the bimolecular channels 1a, 1b, or 1c. The early transition metal ions, Sc^+, Ti^+, V^+, Y^+, Zr^+, Nb^+, La^+, Hf^+, Ta^+, and W^+, and two main group ions, Ge^+ and As^+, react efficiently with SF_6 through both channels (1a) and (1b), forming various products. Only channel (1b) was observed for the relatively slow reaction of Fe^+ with SF_6, whereas all Group 2 metal ions, Ca^+, Sr^+ and Ba^+, reacted efficiently through channels 1a and 1c. No reaction was observed for the other main group metal ions and for a few transition metal ions, that is, Mn^+, Re^+, Os^+, Cd^+ and Hg^+.

The remaining 13 atomic ions studied, that is, Cr^+, Co^+, Ni^+, Cu^+, Zn^+, Mo^+, Ru^+, Rh^+, Pd^+, Ag^+, Ir^+, Pt^+, and Au^+, reacted with SF_6 by slow addition, channel 1d, with effective bimolecular reaction rate coefficients (k) varying from 3.3 × 10^{-12} to 1.7 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} for Ir^+ and Ni^+, respectively. The addition reaction is assumed to occur in a termolecular fashion with helium atoms acting as the stabilizing third body. No attempt was made to measure the pressure dependence of channel 1d since a large range in pressure was not experimentally accessible.

The results of primary reactions are summarized in Table 1. These results include measured rate coefficients (k) and primary product distributions, as well as calculated reaction efficiencies. The reaction efficiency is taken to be equal to the ratio k/k_c where k is the experimentally measured rate coefficient, and k_c is the capture or collision rate coefficient computed using the Langevin model.[55] A typical ion intensity-flow profile is illustrated in Figure 1a for the reaction of Nb^+ with SF_6, and the product ion distribution for the same reaction is presented in the Figure 1b. The initial slope of the Nb^+ ion signal decay in Figure 1a provides a measure of the (effective) bimolecular reaction rate coefficient k. The zero-flow intercepts of the plots of fractional abundance against flow in Figure 1b provide the branching ratios (BR) for the primary reaction products. Figure 2 displays a summary of the results presented in Table 1, that is, primary products and branching ratios, on a periodic table.

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Table 1. Rate Coefficients, *k* (cm^3 $molecule^{-1}$ s^{-1}), Reaction Efficiencies (k/k_c), and Product Ion Branching Ratios for Reactions of Atomic Ions M^+ with SF_6 in Helium at 0.35 ± 0.01 Torr and 295 ± 2 K[a]

M^+	$k/10^{-10}$	k/k_c	MF^+	MF_2^+	MF_3^+	SF^+	SF_2^+	SF_3^+	SF_4^+	SF_5^+	MSF_5^+	$M^+(SF_6)$
Sc^+	6.5	0.63	8	28			43	21				
Y^+	4.5	0.56	22	38			13	27				
La^+	5.3	0.74	10	37			38	15				
Ti^+	9.6	0.96	1	26	7		20	36	10			
Zr^+	6.4	0.80	5	23	22	8	19	18	5			
Hf^+	6.3	0.94	36	20	10	2	14	16	2			
V^{+b}	8.4	0.86		47	3			47	3			
Nb^+	5.4	0.68		26	15		15	29	15			
Ta^+	4.5	0.67	24	26	12		10	24	4			
Cr^+	0.08	0.008										100
Mo^+	0.01	0.001										100
W^+	0.73	0.11		9	9		10	50	6	6		10
Mn^+	<0.001											
Re^+	<0.001											
Fe^+	0.41	0.043						90	3	7		
Ru^+	0.04	0.005										100
Os^+	<0.001											
Co^+	0.66	0.071										100
Rh^+	0.08	0.010										100
Ir^+	0.03	0.005										100
Ni^+	1.7	0.18										100
Pd^+	0.13	0.017										100
Pt^+	0.23	0.035										100
Cu^+	0.85	0.093										100
Ag^+	0.03	0.004										100
Au^+	0.20	0.031										100
Zn^+	0.04	0.004										100
Cd^+	<0.001											
Hg^+	<0.001											
Ca^+	6.3	0.61	84								16	
Sr^+	5.7	0.70	97								3	
Ba^+	6.1	0.85	99								1	
Ge^+	3.1	0.36	34					40	8	18		
As^+	4.5	0.53	2	14				6	3	75		

[a] *k* is the measured reaction rate coefficient for ground-state atomic ions with an estimated accuracy of ± 30%; k_c is the calculated collision rate coefficient (see text). Product branching ratios are expressed as percentage, with an estimated accuracy of ± 5%; the products from excited-state metal ions in the reactions of Cr^+(5%), Mo^+(5%), Mn^+(3%), Os^+(1%), and Ir^+(2%) are not shown. [b] Because of isobaric interference, the product ions VF_m^+ and SF_{m+1}^+ cannot be distinguished in our instrument; the branching ratios in brackets represent one-half of the sum of branching ratios for VF_m^+ and SF_{m+1}^+ ions.

No further reaction was observed for the primary products SF_n^+ and MSF_5^+, produced from channels 1b and 1c, respectively. On the other hand, several MF_m^+ products form channel 1a reacted further with SF_6 to produce MF_{m+k}^+, SF_n^+ (n = 3−5), and $MF_m^+(SF_6)$ ions as secondary products, reaction 2a.

$$MF_m^+ + SF_6 \rightarrow MF_{m+k}^+ + SF_{(6-k)} \qquad k = 1-3 \quad (2a)$$

$$\rightarrow SF_n^+ + MF_{m+(6-n)} \qquad n = 3-5 \quad (2b)$$

$$\rightarrow MF_m^+(SF_6) \quad (2c)$$

We also observed higher-order SF_6 clustering, reaction 3, for Co^+, Ni^+, Cu^+, Ir^+, Pt^+, and Au^+.

$$M^+(SF_6) + SF_6 \rightarrow M^+(SF_6)_2 \quad (3)$$

Figures 3, 4, and 5 display the kinetics data obtained for selected ions of the fourth, fifth, and sixth rows of the periodic table, respectively.

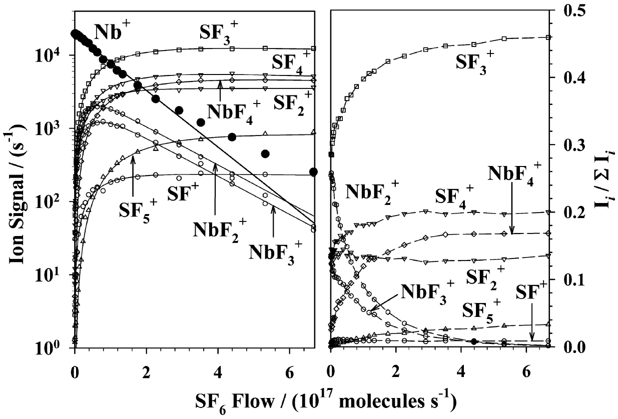


Figure 1. (a) Reactant and product-ion intensities observed for the reactions of Nb^+ with SF_6 as a function of SF_6 flow. The solid lines represent fits to the experimental data points. (b) Plot of fractional abundance of ionized products as a function of SF_6 flow. The zero-flow intercepts provide the Branching Ratios (BR) for the primary reaction products listed in Table 1.

3.1. Early Transition Metal Cations (Group 3−6). Abstraction of single or multiple fluorine atoms resulting in generation of the corresponding ionized metal fluorides (reaction 1a) or partially defluorinated SF_6 cations (reaction 1b) dominated the primary chemistry of the early transition metal ions with SF_6. The occurrence of reaction 1a versus reaction 1b for a particular metal ion depends on the ionization energy (IE) of the MF_m and SF_{6-n} species. Sometimes, both reactions were observed, indicating comparable IEs for the above species. Jiao and Freiser[25] have pointed out that an empty valence d orbital at the metal center can interact with a molecular orbital of SF_6, which have a significant contribution from sulfur 3d orbital, to form an intermediate [M•••SF6]$^+$. This intermediate has a sufficiently

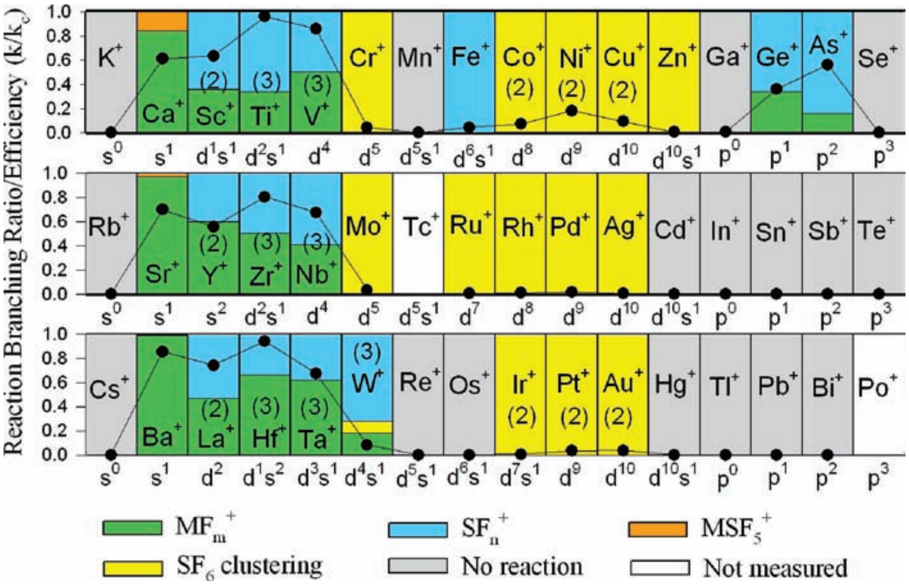


Figure 2. Periodic variations observed in the reaction efficiency (k/k_c), represented by solid circles, for the reactions of ground-state atomic cations with SF_6. Small excited-state effects in the reactions of Cr^+(5%), Mo^+(5%), Mn^+(3%), Os^+(1%), and Ir^+(2%) are not shown. The numbers in parentheses indicate the number of sequential F-atom transfer reactions observed, or the number of sequential SF_6 addition reactions.

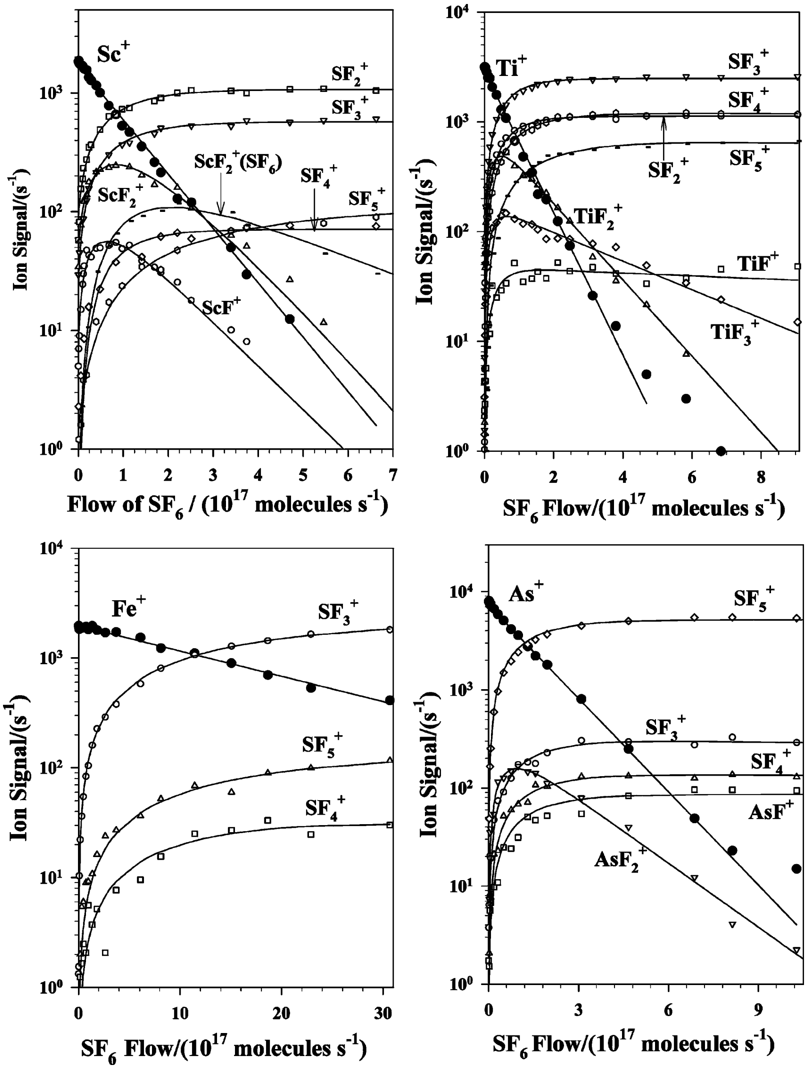


Figure 3. Reactant and product-ion intensities observed for the reaction of the fourth-row ions Sc^+, Ti^+, Fe^+, and As^+ with SF_6 as a function of SF_6 flow in helium buffer gas at 0.35 Torr and 295 K.

long lifetime to allow metal insertion, sequential F atom transfer, and elimination to occur. The reaction mechanism can be expressed by Scheme 1.

Most of the primary reactions of the early transition metals can thus be described as single or multiple F-atom transfer, with or without an electron transfer upon product separation. The following primary reactions were observed for Group 3, 4, and 5 metal ions (again, the nature of the neutral products, not observed experimentally, is uncertain and may involve further dissociation):

$$M^+ + SF_6 \rightarrow MF^+ + SF_5 \quad (4a)$$

$$\rightarrow MF + SF_5^+ \quad (4b)$$

$$M^+ + SF_6 \rightarrow MF_2^+ + SF_4 \quad (5a)$$

$$\rightarrow MF_2 + SF_4^+ \quad (5b)$$

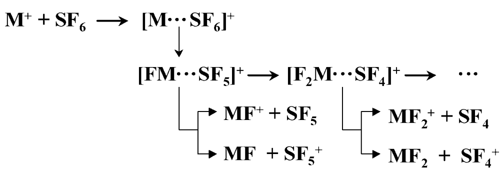
$$M^+ + SF_6 \rightarrow MF_3^+ + SF_3 \quad (6a)$$

$$\rightarrow MF_3 + SF_3^+ \quad (6b)$$

$$M^+ + SF_6 \rightarrow SF_2^+ + MF_4 \quad (7)$$

For the ions of Groups 3, 4, and 5, the ground-state electronic configuration is d^is^j with $i \leq 4$, so that all ions

Scheme 1



have at least one empty d orbital. According to Jiao and Fresier, these early transition metal ions should react very efficiently with SF_6. Our results for the reactions of early transition metal ions with SF_6 are listed in Table 1. The primary product distribution (branching ratios) of MF_m^+ and SF_n^+ ions from reactions 4a to 7 are also included. Assuming that only exothermic or thermoneutral reactions can be observed under our experimental conditions, for the F-atom abstraction reactions to occur efficiently, the F-atom affinity (FA) of the metal ions, FA(M^+), should be higher than that of SF_5, that is, FA(SF_5) = 93.6 kcal mol^{-1}.[56] The F-atom affinities are available for several metal monocations either from theory or experiment and are listed in Table 2. A plot of reaction efficiency (k/k_c) versus F-atom affinity is shown in Figure 6. As indicated in this figure, the metal ions for which FA(M^+) > 93.6 kcal mol^{-1} react with SF_6 very

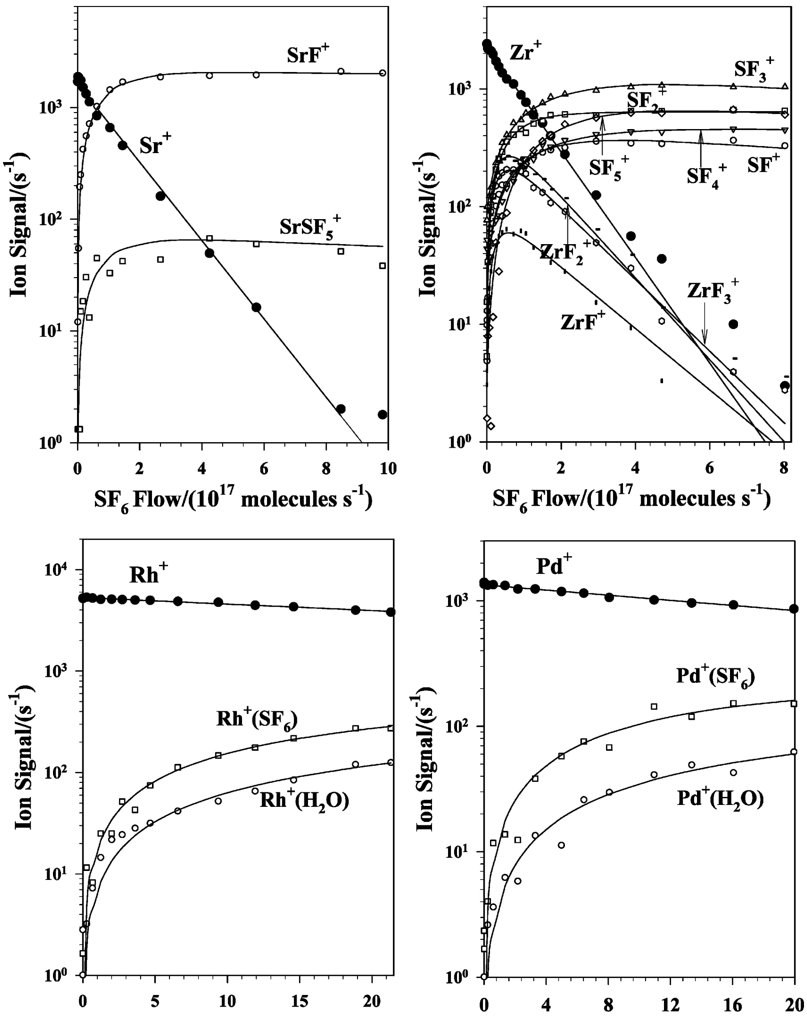


Figure 4. Reactant and product-ion intensities observed for the reaction of the fifth-row ions Sr^+, Zr^+, Rh^+, and Pd^+ with SF_6 as a function of SF_6 flow in helium buffer gas at 0.35 Torr and 295 K.

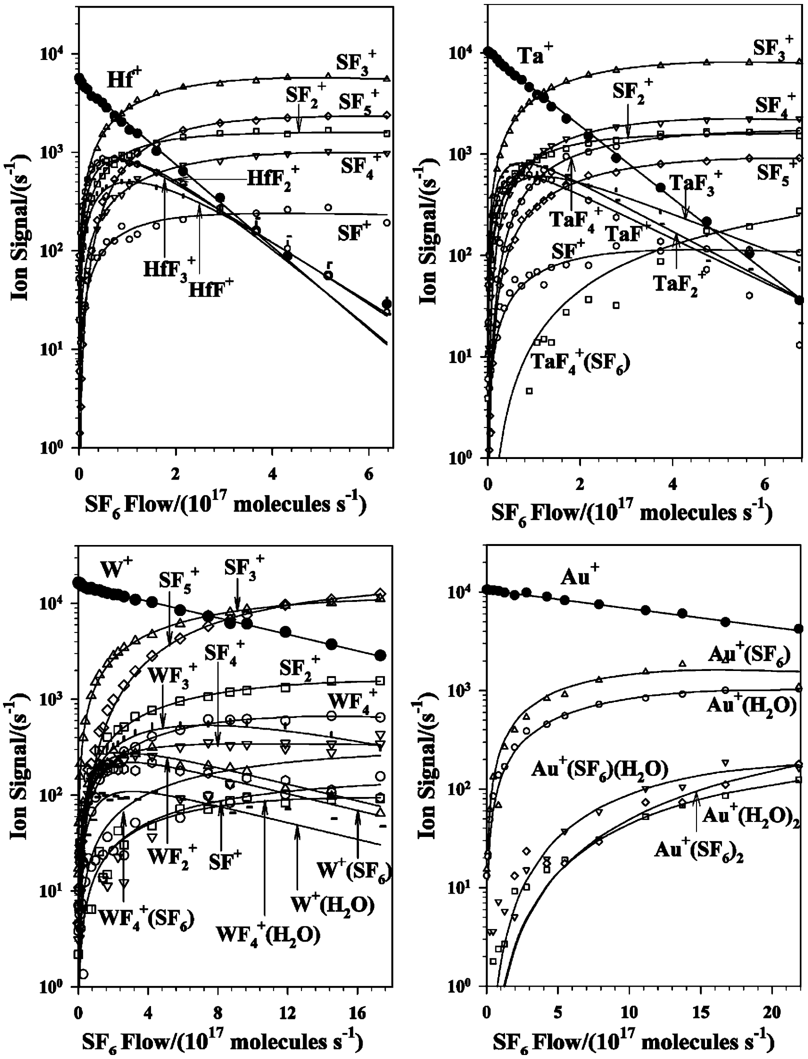


Figure 5. Reactant and product-ion intensities observed for the reaction of the sixth-row ions Hf^+, Ta^+, W^+, and Au^+ with SF_6 as a function of SF_6 flow in helium buffer gas at 0.35 Torr and 295 K.

Table 2. F-Atom Affinities, $D°[F\text{-}M^+]$ in kcal mol^{-1}, for Some Metal Cations[a]

M^+	$FA(M^+)$	T/K	ref.
Ca^+	133.0	298	56
Sr^+	139.8	298	56
Ba^+	153.1	298	56
Sc^+	150.2	298	25
La^+	174.9	0	60
Ti^+	118 ± 9	298	61
Cr^+	73	0	62
Fe^+	92.5 ± 7.5	0	63
Co^+	91.9	0	64
Cu^+	76.2	0	65
Au^+	18	0	66

[a] $D°[F\text{-}SF_5] = 93.6$ kcal mol^{-1}, from ref 56.

efficiently ($k/k_c > 0.5$), while the other ions react at much lower rates ($k/k_c < 0.2$).

For Group 3 cations, Sc^+, Y^+, and La^+, the primary products are MF^+, MF_2^+, SF_2^+, and SF_3^+, produced from reactions 4a, 5a, 6b, and 7, respectively. The ionization energies[56] of SF_5 (9.6 ± 0.5 eV) and SF_4 (12.0 ± 0.3 eV) are significantly larger than those of the MF species, ScF (6.5 ± 0.3 eV), YF (6.3 ± 0.3 eV), and LaF (6.3 ± 0.3 eV), and MF_2, ScF_2 (7.0 ± 0.3 eV), YF_2 (7.0 ± 0.3 eV), and LaF_2 (6.8 ± 0.3 eV). Therefore, reactions 4a and 5a are

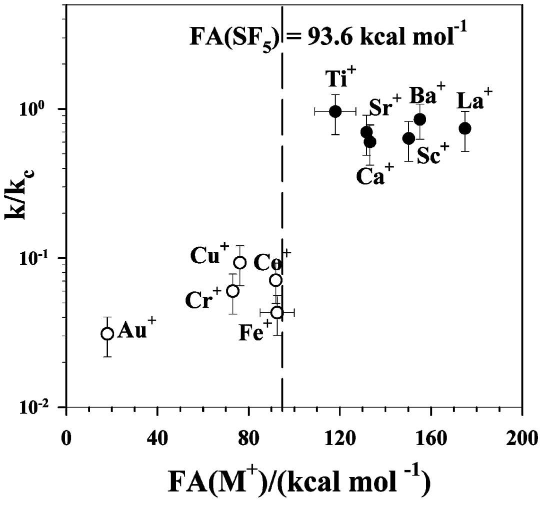


Figure 6. Dependence of the reaction efficiency (k/k_c) on the F-atom affinity of the atomic metal ions. Reactions on the right of the dashed line with dark symbols are F-atom abstraction reactions with single F-atom transfer being exothermic, whereas those on the left with hollow symbols are those for which F-atom transfer is endothermic.

thermodynamically more favorable compared to 4b and 5b, and the branching ratios for MF^+ and MF_2^+ ions should be significantly larger than those of SF_5^+ and SF_4^+ ions, respectively, in accordance with Stevenson's rule.[57] Our experimental results were consistent with these predictions, as we did not observe any SF_5^+ or SF_4^+ ions to be produced through primary reactions of Sc^+ and La^+ with SF_6. Because of the existence of isobaric ions, Y^+ (88.906 amu) versus SF_3^+ (88.967 amu), the YF^+/SF_4^+ and YF_2^+/SF_5^+ pairs are indistinguishable in our instrument. However, on the basis of the ionization energies listed above, the main products of the primary reactions 4a and 5a for Y^+ are assumed to be YF^+ and YF_2^+, respectively, as opposed to SF_5^+ and SF_4^+. We did not observe any MF_3^+ or MF_4^+ ions for M = Sc, Y, and La, consistent with the fact that the highest oxidation number for Group 3 metals is +3.

Although reaction 6a is significantly more exothermic than reaction 7 for Sc^+ ion,[25] we observed that the branching ratio for SF_2^+ (42%) is larger than that of SF_3^+ (21%). Jiao and Freiser[25] speculated that SF_2^+ might be produced from the dissociation of SF_3^+ product, which is formed from reaction 6a. However, the reaction profile of Sc^+ (Figure 3) and our product ratio analysis clearly indicate that SF_2^+ is a primary product formed directly from reaction 7. The large branching ratio for SF_2^+ (42%) can be explained by the conservation of electron spin in the reaction; because the ground-state $Sc^+(^3D)$ has two unpaired electrons, reaction 6a to form SF_3^+(singlet) and ScF_3(singlet) is spin-forbidden while reaction 7 is spin-allowed.

The primary products ScF_2^+, YF_2^+, and LaF_2^+ reacted further with SF_6 by termolecular addition, reaction 2c, to form $MF_2^+(SF_6)$ clusters. Small amounts of SF_4^+ and SF_5^+ ions were also observed as secondary products for Sc^+, consistent with the findings of Jiao and Freiser.[25]

For Group 4 cations, Ti^+, Zr^+, and Hf^+, all primary products of reactions 4a−7 except SF_5^+ (4b) were observed, and the results are listed in Table 1. The ionization energy[56] of SF_3 (8.18 ± 0.07 eV) is smaller than that of TiF_3 (10.8 ± 0.3 eV) and slightly larger than that of ZrF_3 (7.5 ± 0.3 eV), which is reflected in the relative branching ratios of these ions in Table 1; the relative branching ratios (SF_3^+/TiF_3^+) and (SF_3^+/ZrF_3^+) are 5 and 0.8, respectively. No MF_4^+ ions were observed for M = Ti, Zr, and Hf, consistent with the fact that the highest oxidation number for Group 4 metals is +4.

The major secondary product of the reactions of Ti^+, Zr^+, and Hf^+ with SF_6 is the SF_5^+ ion. We also found that SF_3^+ and SF_4^+ are produced by both primary and secondary reactions. For the Ti^+ and Zr^+ ions, the following reactions are exothermic[56] and likely to be responsible for the formation of secondary product ions.

$$MF_2^+ + SF_6 \rightarrow MF_3 + SF_5^+ \qquad M = Ti, Zr \qquad (8a)$$

$$\rightarrow MF_4 + SF_4^+ \qquad M = Ti, Zr \qquad (8b)$$

$$\rightarrow MF_4 + SF_3^+ + F \qquad M = Ti, Zr \qquad (8c)$$

Reactions 8a, 8b, and 8c for TiF_2^+ are exothermic by 105, 102, and 109 kcal mol^{-1}, respectively, while for ZrF_2^+ they are exothermic by 112, 157, and 164 kcal mol^{-1}, respectively.[56] There is no thermochemical data available for the HfF_2^+ ion, and the exothermicity of the above reactions for HfF_2^+ cannot be evaluated.

For Group 5 cations, V^+, Nb^+, and Ta^+, all primary products of reactions 4a−7 except SF_5^+ (4b) were observed. Because of the existence of isobaric ions, V^+ (50.944 amu) versus SF^+ (50.970 amu), the VF^+/SF_2^+, VF_2^+/SF_3^+, and VF_4^+/SF_5^+ pairs were indistinguishable in our instrument. We also observed NbF_4^+, TaF_4^+, and VF_4^+ (or SF_5^+) ions as the main secondary products formed from the reactions of VF_m^+, NbF_m^+, and TaF_m^+ ($m \leq 3$) with SF_6, reaction 2a. This is clearly indicated for Nb^+ in Figure 1b; the relative signal intensity of NbF_4^+ increases with increasing flow, while those of NbF_2^+ and NbF_3^+ decrease. We also observed that SF_3^+ is produced by both primary and secondary reactions of Nb^+ and Ta^+ with SF_6. However, there is not enough thermochemical data available to evaluate the enthalpies of the reactions yielding these secondary products. Another higher order reaction of Group 5 ions was the termolecular addition of SF_6 to TaF_4^+, reaction 2c. The formation of VF_4^+, NbF_4^+, and TaF_4^+ ions has been reported previously from the reactions of bare metal ions with hexafluorobenzene[42,43] or other fluorocarbons.[58]

The Group 6 cations, Cr^+, Mo^+, and W^+, react with SF_6 with relatively low rates. The ground-state electronic configurations of Cr^+, Mo^+, and W^+ are $3d^5$, $4d^5$, and $6s^15d^4$, respectively. Because of the special stability of the half-filled valence shell orbitals,[59] the ground-state Cr^+ and Mo^+ react with SF_6 very slowly (k/k_c < 0.01). In an ICP ion source at 5500 K temperature, the $4s^13d^4$ excited state of Cr^+ has a population of about 16%, and the $5s^14d^4$ excited state of Mo^+ has a population of about 14% at that temperature.[36] By inspecting the reaction profiles of Cr^+ and Mo^+ ions, we found traces of excited states (∼ 5%) to be present. Excited Cr^+ ions react with SF_6 to produce SF_3^+, SF_5^+, and $CrSF_5^+$, whereas excited Mo^+ ions produce SF_3^+, SF_5^+, and SF_2^+. Although the overall reaction $Mo^+ + SF_6 \rightarrow MoF_3 + SF_3^+$ is exothermic by 106 kcal mol^{-1},[56] only excited-state Mo^+ ions appear to have enough energy to overcome the reaction barrier. The ground-state Cr^+ and Mo^+ ions react very slowly by termolecular SF_6 addition, reaction 1d. The other ion of Group 6, W^+, has an empty d orbital in its ground electronic state and is significantly more reactive toward SF_6 (k/k_c = 0.11). The W^+ ions react with SF_6 through various channels, 1a, 1b, and 1d, and as many as seven primary products were observed (Table 1). The major primary product of the reaction between W^+ and SF_6 is SF_3^+(50%), and the higher-

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order products are SF_5^+, WF_4^+, and $WF_4^+(SF_6)$, see Figure 5.

The reaction efficiencies of Group 3, 4, and 5 ions (excluding Hf^+) with SF_6 reported previously by Jiao and Fresier using the FT-ICR technique[25] are systematically smaller than our k/k_c values obtained using the ICP-SIFT/MS technique. For example, k/k_c for the reaction of Sc^+ with SF_6 in the FT-ICR experiment was 0.27, whereas a value of 0.63 was obtained for the same reaction in our experiments. The reason for this discrepancy might be associated with the reaction environment and instrument. In our ICP-SIFT experiment, reaction occurs in helium buffer gas at 0.35 ± 0.01 Torr, whereas in the FT-ICR experiment the reaction occurs in a reaction cell containing SF_6 at a pressure of 2×10^{-7} Torr. Jiao and Fresier[25] have also reported "product distributions" at 1 s. reaction time for reactions of some early transition metal ions with SF_6 ($\sim 2 \times 10^{-7}$ Torr). These distributions, measured at a fixed reaction time, will be influenced by any secondary reactions that may occur with SF_6 and so will not be true primary product distributions if secondary reactions occur within 1 s. The branching ratios reported in Table 1 are true primary product distributions as they are determined from to zero-flow intercepts of the plots of fractional abundance against the flow of reactant. There is reasonable agreement between the two reported branching ratios only for non-reactive primary products. For example, the SF_3^+ branching ratios in the reactions of Sc^+, Y^+, and La^+ ions with SF_6 (Table 1) are 21%, 27%, and 15%, respectively, and the corresponding "product distributions" reported by Jiao and Freiser[25] were 20%, 35%, and 10%, respectively.

3.2. Late Transition Metal Cations (Group 7−12). Unlike Group 3−5 ions, most late transition-metal ions react with SF_6 by slow termolecular addition ($k/k_c < 0.2$), with helium atoms acting as the stabilizing third body.

$$M^+ + SF_6 + He \rightarrow M^+(SF_6) + He \tag{9}$$

The efficiencies of the above reaction increase from Group 7 to 10, and decrease from Group 10 to 12. Reaction 9 was not observed for Mn^+, Re^+, Fe^+, Os^+, Cd^+, and Hg^+ ions. On the other hand, second-order SF_6 addition, reaction 3, was observed exclusively for the ions of Group 9−11 in the fourth and sixth rows of the periodic table, that is, Co^+, Ni^+, Cu^+, Ir^+, Pt^+, and Au^+.

The only late transition-metal ion that expresses a bimolecular reaction with SF_6 is Fe^+, which reacts through channel 1b, although the reaction is not very efficient ($k/k_c = 0.04$). The dominant product of this reaction is SF_3^+(90%), while SF_4^+(3%) and SF_5^+(7%) are minor products. The linearity observed in the reaction profile of Fe^+ with SF_6 (Figure 3) suggests that any excited states that may be present react with a similar rate. Jiao and Freiser[25] also have observed the products SF_3^+ and SF_5^+ for the same reaction. From the available thermochemical data,[56] we find that reaction 10 is exothermic by 118 kcal mol^{-1}.[56]

$$Fe^+ + SF_6 \rightarrow FeF_3 + SF_3^+ \tag{10}$$

So a likely reason for the low efficiency of this reaction is the existence of a kinetic barrier. This channel appears to be the most exothermic of all possible channels, although the enthalpy change for the channel leading to FeF^+ could not be determined because of the unknown enthalpy of formation of this ion.

3.3. Main Group Metal Cations. Reactions of SF_6 were measured with main group cations in the fourth, fifth, and sixth rows of the periodic table. The only main group cations that react with SF_6 are Ge^+, $As^{+,}$ and the Group 2 metal ions, Ca^+, Sr^+, and Ba^+. The reactions efficiencies (k/k_c) for Ge^+ and As^+ ions were 0.36 and 0.53, respectively, and those for the Group 2 ions were in the 0.61−0.85 range.

High reactivities of Ge^+ and As^+ ions toward other neutral molecules, for example, with CH_3F, have been reported previously.[38] Reactions of these two ions with SF_6 are similar to those of the early transition-metal ions (Group 3−5) so that MF_m^+ and SF_n^+ are the primary products derived from channels 1a and 1b. The primary products for Ge^+ and As^+ and their branching ratios are listed in Table 1; the major difference between these ions and those of Group 3−5 is in the formation of SF_5^+ as a significant primary product. The branching ratios of SF_5^+ in the reactions of Ge^+ and As^+ with SF_6 are 18% and 75%, respectively, whereas SF_5^+ is only a secondary product for the Group 3−5 ions. No secondary or higher-order reaction was observed for Ge^+, but the product ratio analyses revealed that SF_5^+ is produced also as a secondary product for As^+ from the following reaction.

$$AsF_2^+ + SF_6 \rightarrow AsF_3 + SF_5^+ \tag{11}$$

From the available thermochemical data, reaction 11 was found to be exothermic by 58.7 kcal mol^{-1}.[56]

For Group 2 metal ions, the dominant primary product is MF^+, produced from the following bimolecular reaction.

$$M^+ + SF_6 \rightarrow MF^+ + SF_5 \qquad M = Ca, Sr, Ba \tag{12}$$

Reaction 12 is exothermic for Ca^+, Sr^+, and Ba^+ ions by 39.4, 46.2, and 59.5 kcal mol^{-1}, respectively, because the $F\text{-}M^+$ bonds (M = Ca, Sr, Ba) are significantly stronger than the $F\text{-}SF_5$ bond (see Table 2). The CaF^+, SrF^+, and BaF^+ product ions have branching ratios of 84%, 97%, and 99%, respectively. The only other primary product for Group 2 metal ions is MSF_5^+, produced by reaction 1c. No secondary or higher-order reactions were observed for these ions.

3.4. Reactions with Water Impurity. We also observed reactions with the water impurity (<5 ppm) in the helium buffer gas. These reactions were observed exclusively for the late transition-metal ions that form $M^+(SF_6)$ clusters. Figures 4 and 5 display the formation of $M^+(H_2O)$ cluster ions parallel to $M^+(SF_6)$ for the Rh^+, Pd^+, and Au^+ ions. Since the concentration of H_2O in the helium buffer gas is very small (ppm) and the direct water clustering reactions for the bare metal ions Rh^+, Pd^+, and Au^+ are not efficient ($k/k_c < 0.01$),[32] the formation of $M^+(H_2O)$ clusters in these

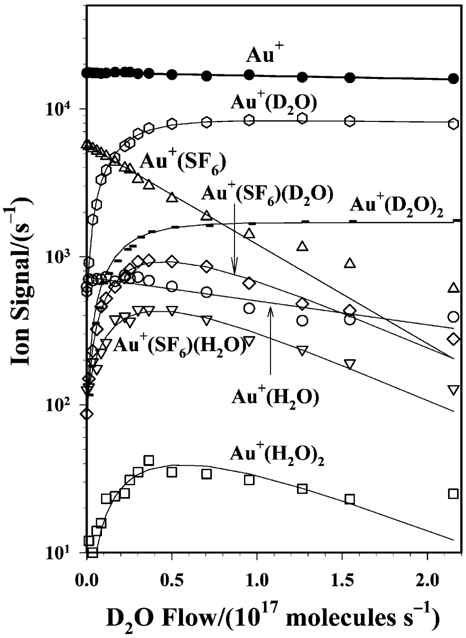

Figure 7. Profile of the reaction between D_2O and the product ions of the Au^+/SF_6 reaction, see text.

Table 3. Rate Coefficients (cm^3 $molecule^{-1}$ s^{-1}), Reaction Efficiency (k/k_c), and the Standard Free Energy Changes ($kcal\ mol^{-1}$) for Sequential SF_6 Addition to Metal Cations at 295 ± 2 K

	$M^+(SF_6)$			$M^+(SF_6)_2$		
M^+	k^a	k/k_c [b]	$-\Delta G°$ [c]	k^a	k/k_c [b]	$-\Delta G°$ [c]
Co^+	6.6×10^{-11}	0.071	9.5	4.0×10^{-11}	0.061	8.6
Ni^+	1.7×10^{-10}	0.18	10.1	7.9×10^{-11}	0.12	9.5
Cu^+	8.5×10^{-11}	0.093	10.0	3.9×10^{-11}	0.059	8.8
Zn^+	4.0×10^{-12}	0.004	6.6			
Ru^+	4.0×10^{-12}	0.005	6.7			
Rh^+	8.0×10^{-12}	0.010	7.5			
Pd^+	1.3×10^{-11}	0.017	8.1			
Ag^+	3.0×10^{-12}	0.004	6.3			
Pt^+	2.3×10^{-11}	0.035	8.6	4.0×10^{-11}	0.067	8.7
Au^+	2.0×10^{-11}	0.031	8.6	6.3×10^{-12}	0.010	7.4

[a] Measured reaction rate coefficient with an estimated accuracy of ± 30%. [b] Reaction efficiency, k_c is the calculated collision rate coefficient (see text). [c] The standard free energy changes with an uncertainty estimated to be no more than 0.3 $kcalmol^{-1}$.

experiments is attributed to the following H_2O-SF_6 exchange reaction.

$$M^+(SF_6) + H_2O \rightarrow M^+(H_2O) + SF_6 \qquad (13)$$

Bimolecular "solvent switching reactions" of type 13 are often fast and can proceed near the collision rate.[67]

We performed a separate experiment to confirm the occurrence of reaction 13 for the $M^+ = Au^+$. In this experiment, constant amounts of SF_6 gas were added into the first sample inlet to form the $Au^+(SF_6)$ cluster upstream of the flow tube. D_2O was then added downstream, and variations in the ion signals were measured with increasing flow of D_2O. Figure 7 displays the reaction profile for the SF_6/D_2O exchange. It is clear from this reaction profile that $Au^+(D_2O)$ is produced quite rapidly from the $Au^+(SF_6)$ cluster ion by SF_6/D_2O exchange rather than by addition of D_2O to Au^+; the Au^+ ion signal is almost constant. The exchange 14a appears to compete with the simple addition of D_2O (14b) as a minor (<20%) channel. We measured the rate coefficient for reaction 14a to be 8×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, which corresponds to a reaction

$$Au^+(SF_6) + D_2O \rightarrow Au^+(D_2O) + SF_6 \qquad (14a)$$

$$\rightarrow Au^+(SF_6)(D_2O) \qquad (14b)$$

efficiency of $k/k_c = 0.4$; the effective bimolecular rate coefficient for the direct formation of $Au^+(D_2O)$ from Au^+ and D_2O in 0.35 Torr of helium buffer gas has been reported[32] to be 5.8×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and so is smaller than this value by 2 orders of magnitude. The rapid occurrence of reaction 14a suggests that $D(Au^+\text{-}D_2O) > D(Au^+\text{-}SF_6)$ so that $D(Au^+\text{-}SF_6) < 40 \pm 2$ kcal mol^{-1}.[68] Figure 7 also displays the occurrence of the conversion of $Au^+(SF_6)(D_2O)$ to $Au^+(D_2O)_2$ and some conversion of $Au^+(H_2O)$ to $Au^+(D_2O)$ by switching reactions with D_2O.

3.5. Equilibrium Kinetics and Standard Free Energies of Association. Equilibrium analyses performed on the kinetic results indicate that equilibrium is attained in

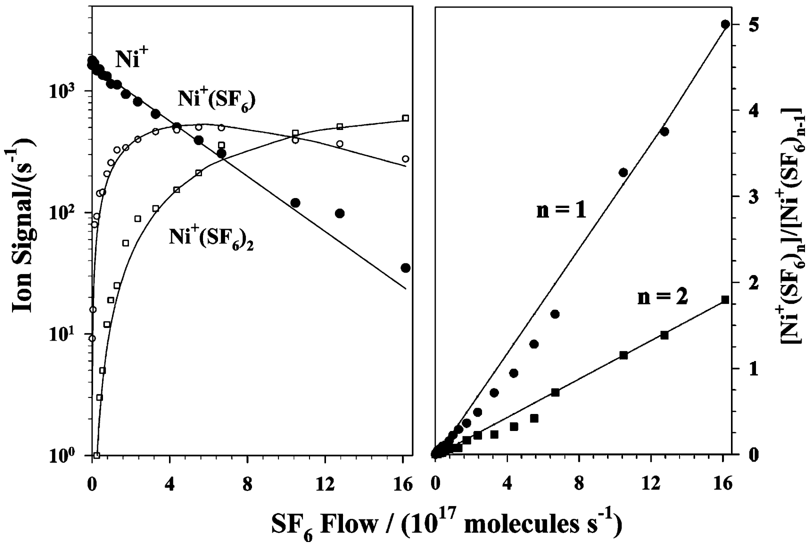

Figure 8. Variation observed in the ion signal ratio of $I[Ni(SF_6)_n]^+/I[Ni(SF_6)_{n-1}]^+$ (n = 1,2) for the sequential addition of SF_6 to Ni^+ with the flow rate of SF_6.

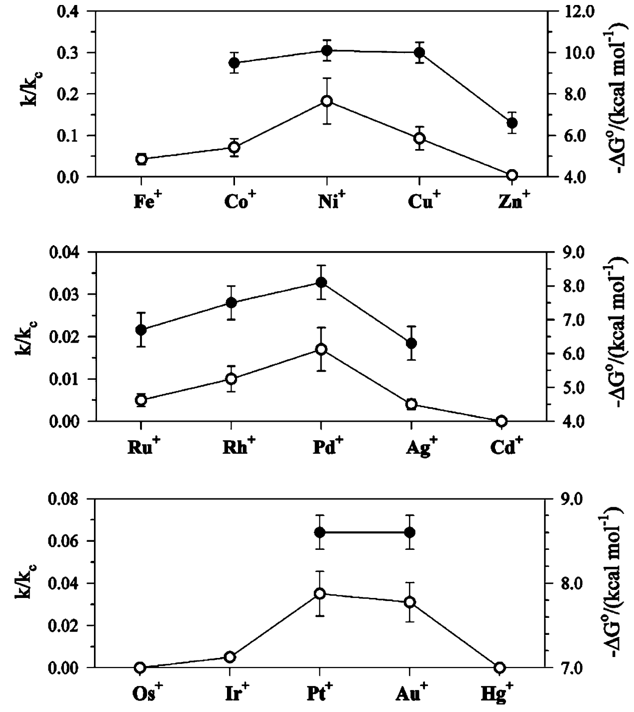

Figure 9. Variations observed in the reaction efficiency (open circles) and the standard free energy change (solid circles) for SF_6 addition with the configuration of the atomic cations.

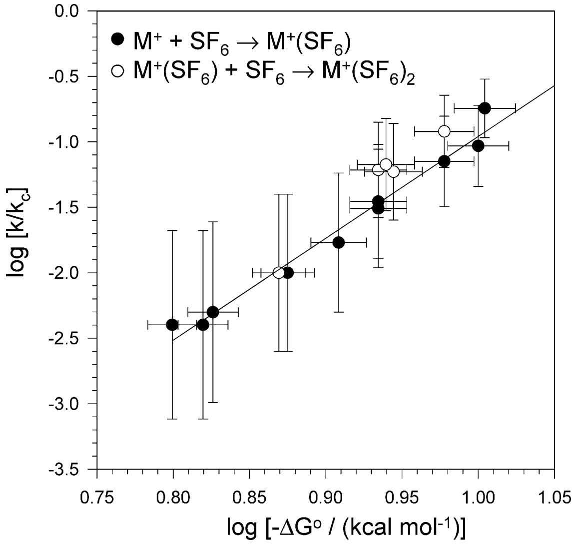

Figure 10. Dependence of the reaction coefficient, k/k_c, on the relative free energy change, $-\Delta G°$. The fitted equation is $\log[k/k_c] = -8.7 + 7.8 \log[-\Delta G°/(\text{kcal mol}^{-1})]$. The error bars are assigned according to a 30% uncertainty in $\log[k/k_c]$ and a 2% uncertainty in $\log[-\Delta G°]$.

almost all the SF_6 addition reactions. These analyses are based on plots of product-to-reactant ion signal ratios as a function of SF_6 flow. Equilibrium is achieved when this plot achieves linearity, namely, when $[M^+(SF_6)_n]/[M^+(SF_6)_{n-1}] = K[SF_6]$ where K is the equilibrium constant. The equilibrium kinetics for the association reactions that were observed was well behaved, and the ion-signal ratio plots were linear. This is demonstrated in Figure 8 for the sequential addition of two SF_6 molecules to Ni^+. Table 3 lists the reaction rate coefficients, reaction efficiencies, and standard free energies for the addition of up to two molecules of SF_6 to various M^+ ions.

As far as we are aware, the reaction rate coefficients, reaction efficiencies, and standard free energy changes for SF_6 addition that are reported in Table 3 are generally unknown from previous measurements and calculations. Figure 9 explores the periodic variation in the values of the measured reaction efficiencies and the standard binding free energies for the addition of SF_6 to M^+ observed at 295 ± 2 K. There is a clearly periodic correspondence in the trends of the reaction efficiency and standard binding free energy across three periods of the periodic table. The log/log plot in Figure 10 displays the dependence of the reaction efficiencies (k/k_c) of one and two SF_6 additions to the bare metal cations on the relative standard free energy change $\Delta G°/(\text{kcal mol}^{-1})$. The dependence fits the equation $\log[k/k_c] = -8.7 + 7.8 \log[-\Delta G°/(\text{kcal mol}^{-1})]$ for the addition of one SF_6 molecule. The plot versus $\log \Delta H°$ would look similar (but shifted in the intercept) if the entropy change in these addition reactions is independent of the metal cation, as is likely to be the case. An increase in the efficiency of ligation is expected as the binding enthalpy or free energy increases as this increases the lifetime of the intermediate adduct (in the two-step association mechanism) that is collisionally stabilized by the helium buffer gas atoms. The efficiency of ligation will depend on the lifetime of the intermediate $[M^+(SF_6)]^*$ against dissociation back to reactants which in turn depends on $D(M^+\text{-}SF_6)$ according to $\tau = \tau_0\{(D + 3RT)/3RT\}^{s-1}$ where s is the number of degrees of freedom in the transient intermediate $[M^+(SF_6)]^*$ effective in intramolecular energy redisposition.[69] The slope of the log/log plot in Figure 10 provides a measure of s. If the slope is taken to be equal to $s-1$, then the effective number of degrees of freedom is $s = 8.8$ which is slightly less than half of the total number of degrees of freedom for $[M^+(SF_6)]^*$ which contains 8 atoms. As expected from the increase in the number of degrees of freedom of the transient intermediate, the value of $s = 11$ that can be estimated from Figure 10 for the second addition of SF_6 is somewhat larger than $s = 8.8$ obtained for the first addition.

4. Conclusions

The results of our systematic study on the reactivity of 46 metal monocations with SF_6 have revealed trends across and down the periodic table with regard to both the type of chemistry and the reaction efficiency. Reactions of early transition-metal ions with SF_6 are very efficient ($k/k_c > 0.5$) and are dominated by multiple F-atom transfer resulting in formation of MF_m^+ ($m \leq 3$) and SF_n^+ ($n \leq 4$) ions as primary products. Reactions of late transition-metal ions with SF_6 are significantly less efficient and are dominated by SF_6 addition. Reactions of Ge^+, As^+, and the Group 2 metal ions with SF_6 are very efficient, while all other main group cations are inert toward SF_6. Several MF_m^+ ions were observed to react further with SF_6 to

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produce MF_{m+k}^+, SF_n^+, and $MF_m^+(SF_6)$ as secondary products. Primary and secondary adduct formation with atomic ions exhibits equilibrium kinetics under the conditions of the SIFT experiments, and the standard free energy change for SF_6 addition is found to correlate with the efficiency of addition.

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(69) See, for example, Tonkyn, R.; Roman, M.; Weisshaar, J. C. *J. Phys. Chem.* **1988**, *92*, 92.