Inorg. Chem. **2006**, *45*, 7856–7863

Inorganic Chemistry
Article

Gas-Phase Reactions of Atomic Lanthanide Cations with Sulfur Hexafluoride: Periodicity in Reactivity

Ping Cheng 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, Canada M3J 1P3

Received June 5, 2006

Room-temperature reactions of sulfur hexafluoride (SF_6) have been surveyed systematically with atomic lanthanide cations (Ln^+, excluding Pm^+) in the gas phase, using an inductively coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer. Rate coefficients and product distributions were measured in helium at a pressure of 0.35 Torr and temperature of 295 K. All the Ln^+ cations were observed to react efficiently ($k/k_c > 0.24$) and predominantly by single and multiple F atom and fluoride abstraction to produce both LnF_n^+ and SF_n^+(where $n =$ 1, 2, 3). The observed periodic trend in reaction efficiency along the lanthanide row matches the periodic trend in the electron-promotion energy of the Ln^+ cation. A remarkable Arrhenius-like correlation is observed for the dependence of reactivity on promotion energy: the early and late lanthanide cations exhibit effective temperatures of 45 500 and 14 000 K, respectively. SF_n^+ product ions are observed to be unreactive with SF_6, whereas up to two molecules of SF_6 have been observed to add to LnF_n^+ product ions under the experimental operating conditions of the ICP/SIFT tandem mass spectrometer.

1. Introduction

Sulfur hexafluoride (SF_6) is a remarkable molecule, in that it is often exploited, because it is rather inert chemically and electrically;[1−13] however, at the same time, it is also used as a source of F atoms in chemical lasers, as well as in plasma etching technology.[5,14] The S−F bond is relatively weak: $D(F-SF_5) = 93.6 \pm 0.1$ kcal mol^{-1}.[15] Mass spectrometer experiments have shown that activation of this bond can be achieved in the gas phase with a variety of different atomic ions. For example, Fourier transform ion cyclotron resonance (FT−ICR) mass spectrometer measurements performed by Jiao and Freiser[16] have shown that eight early atomic transition-metal cations react efficiently with SF_6 via single and multiple F-atom abstraction. These authors surmised that at least one empty valence d orbital with the proper symmetry is needed by the atomic cation for reaction to occur with SF_6. Recently, Gibson et al.[17] found that the bare U^+ cation reacts efficiently (40%) with SF_6 to produce both UF_n^+ ($n = 1, 2, 3, 4$) and SF_n^+ ($n = 1, 2, 3$) cations in the gas phase. The measured UF^+/SF_6 reaction rate was essentially the same as that for U^+/SF_6; however, both UF_2^+ and UF_3^+ were observed to be relatively unreactive. Gibson also reported the observation of the formation of ions of the type LnF^+ and LnF_2^+ in the reactions of the lanthanide cations Tb^+ and Ho^+ with SF_6.[18] Experiments by Adams et al.[19]

---

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

(1) Babcock, L. M.; Streit, G. E. *J. Chem. Phys.* **1981**, *74*, 5700.
(2) Masuoka, T.; Samson, J. A. R. *J. Chem. Phys.* **1981**, *75*, 4946.
(3) Stanski, T.; Adamczyk, B. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *46*, 31.
(4) Johnstone, W. M.; Newell, W. R. *J. Phys. B−At. Mol. Opt. Phys.* **1991**, *24*, 473.
(5) Roque, M. B.; Siegel, R. B.; Martus, K. E.; Tarnovsky, V.; Becker, K. *J. Chem. Phys.* **1991**, *94*, 341.
(6) Creasey, J. C.; Jones, H. M.; Smith, D. M.; Tuckett, R. P.; Hatherly, P. A.; Codling, K.; Powis, I. *Chem. Phys.* **1993**, *174*, 441.
(7) Li-Aravena, F.; Saporoschenko, M. *J. Chem. Phys.* **1993**, *98*, 8888.
(8) Jones, A. B.; Woodward, C. A.; Winkel, J. F.; Stace, A. J. *Int. J. Mass Spectrom. Ion Process.* **1994**, *133*, 83.
(9) Liu, J.; Raju, G. R. G. *IEEE Trans. Dielectr. Electr. Insul.* **1994**, *1*, 520.
(10) Evans, M.; Ng, C. Y.; Hsu, C. W.; Heimann, P. *J. Chem. Phys.* **1997**, *106*, 978.
(11) Coquel, J. M.; Hunt, M. R. C.; Siller, L.; Palmer, R. E. *J. Appl. Phys.* **1998**, *84*, 4603.
(12) Victor, D. G.; MacDonald, G. J. *Climatic Change* **1999**, *42*, 633.
(13) Singh, R. K.; Hippler, R.; Shanker, R. *Phys. Rev. A: Atom. Mol. Opt. Phys.* **2003**, *67*, 022704/1.
(14) Flamm. D. L.; Donelly, V. M. *Plasma Chem. Plasma Process.* **1981**, *1*, 137.
(15) http://webbook.nist.gov/chemistry/.
(16) Jiao, C. Q.; Freiser, B. S. *J. Am. Chem. Soc.* **1993**, *115*, 6268.
(17) Jackson, G. P.; Gibson, J. K.; Duckworth, D. C. *J. Phys. Chem. A* **2004**, *108*, 1042.
(18) Gibson, J. K. *J. Fluor. Chem.* **1996**, *78*, 65.
(19) Williams, T. L.; Babcock, L. M.; Adams, N. G. *Int. J. Mass Spectrom.* **1999**, *187*, 759.

10.1021/ic061000o CCC: $33.50

showed that some nonmetallic atomic ions (e.g., D^+, He^+, N^+, Ar^+, Ne^+) react with SF_6 via electron transfer to form an unstable $[SF_6^+]^*$ species, followed by fragmentation to SF_5^+, or by F^- ion abstraction.

Gas-phase reactions between atomic lanthanide cations (Ln^+) with SF_6 are relatively unexplored. Investigations with other inorganic and some organic molecules to date have shown that the reactivity of atomic Ln^+ metal cations varies markedly along the 4f series, in terms of both ionic products formed and reaction efficiency.[20−28] The reactivity differences seem to be governed by the accessibility of electronic configurations with two unpaired non-f electrons. The results with N_2O also have revealed intriguing Arrhenius-like dependencies of the reactivity of the Ln^+ cation on the electron promotion energy, with effective temperatures of 22 000 and 6100 K for the early and late lanthanide cations, respectively. Until now, reactions of the Ln^+ cation have been investigated systematically with hydrogen,[29] oxygen,[30] nitrous oxide,[30] alkanes and cycloalkanes,[22,23,31] alkenes,[20−22] alcohols,[26,28,32] benzene and substituted benzenes,[24,33] phenol,[34] orthoformates,[24,35] ferrocene and Fe pentacarbonyl,[36] and methyl fluoride and chloride.[37,38]

Here we report a systematic experimental investigation of S−F bond activation in reactions of all the Ln^+ cations (except Pm^+) with SF_6, using inductively coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometry. Our measurements of the reactions of SF_6 with 46 atomic transition and main-group metal cations using the same instrument will be reported separately.[39]

2. Experimental Section

The experiments were performed with the ICP/SIFT tandem mass spectrometer, which has been described in detail previously.[40,41] The atomic ions were generated within an atmospheric-pressure argon plasma at 5500 K fed with a vaporized solution that contained the lanthanide salt. The ions that emerged from the inductively coupled plasma (ICP) were injected through a differentially pumped sampling interface into a quadrupole mass filter and, after mass analysis, were introduced through an aspirator-like interface into flowing helium carrier gas at a pressure of 0.35 Torr and temperature of 295 ± 2 K. After experiencing $\sim 10^5$ collisions with He atoms, the ions were allowed to react with SF_6 that was added into the flow tube.

The Ln^+ ions emerging from the plasma initially have a Boltzmann internal energy distribution, which is characteristic of the plasma temperature. However, these emerging populations are expected to be downgraded during the ~20 ms duration before entry into the reaction region in the flow tube. Energy degradation can occur by radiative decay as well as by collisions with Ar atoms and the 10^5 collisions with He before entry into the reaction region. The extent to which quenching of any electronically excited states of the Ln^+ cations that may be formed within the ICP is completely uncertain and could be inferred only indirectly from the observed decays of primary ion signals. The observed semilogarithmic decays of the reacting lanthanide cations were invariably linearly, often over as much as four decades of ion depletion, and so were indicative of single-state populations. The many collisions with Ar and He between the source and the reaction region should ensure that the atomic ions reach a translational temperature equal to the tube temperature of 295 ± 2 K prior to entering the reaction region.

Reactant and product ions were sampled at the end of the flow tube with a second quadrupole mass filter and were measured as a function of added reactant. The resulting profiles provide information about reaction rate coefficients and product-ion distributions. Rate coefficients for primary reactions were determined with an uncertainty that was estimated to be less than ±30% from the semilogarithmic decay of the reactant ion intensity, as a function of added reactant.

SF_6 was introduced into the reaction region of the SIFT as a dilute mixture in helium (~10%). The SF_6 was obtained commercially and had high purity (BOC, >99.9% purity).

3. Results and Discussion

The reactions of 14 Ln^+ cations were investigated with SF_6. Both the primary and higher-order chemistries were monitored. Results obtained for the reactions of La^+, Nd^+, Gd^+, and Tb^+ are shown in Figure 1. Table 1 summarizes the measured rate coefficients, reaction efficiencies, and product distributions. The reaction efficiency is considered to be equal to the ratio of k/k_c, where k is the experimentally measured rate coefficient and k_c is the capture or collision rate coefficient. k_c was calculated using the algorithm of the modified variational transition-state/classical trajectory theory

---

(20) Huang, Y.; Wise, M. B.; Jacobson, D. B.; Freiser, B. S. *Organometallics* **1987**, *6*, 346.
(21) Gibson, J. K. *J. Phys. Chem*. **1996**, *100*, 15688.
(22) Schilling, J. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 15.
(23) Cornehl, H. H.; Heinemann, C.; Schroeder, D.; Schwarz, H. *Organometallics* **1995**, *14*, 992.
(24) Gibson, J. K.; Haire, R. G. *Radiochim. Acta* **2001**, *89*, 709.
(25) Heinemann, C.; Schroeder, D.; Schwarz, H. *Chem. Ber*. **1994**, *127*, 1807.
(26) Azzaro, M.; Breton, S.; Decouzon, M.; Geribaldi, S. *Int. J. Mass Spectrom. Ion Process.* **1993**, *128*, 1.
(27) Cornehl, H. H.; Hornung, G.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 9960.
(28) Carretas, J. M.; Marcalo, J.; Pires de Matos, A. *Int. J. Mass Spectrom*. **2004**, *234*, 51.
(29) Elkind, J. L.; Sunderlin, L. S.; Armentrout, P. B. *J. Phys. Chem.* **1989**, *93*, 3151.
(30) Koyanagi, G. K.; Bohme, D. K. *J. Phys. Chem. A* **2001**, *105*, 8964.
(31) Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 3845.
(32) Geribaldi, S.; Breton, S.; Decouzon, M.; Azzaro, M. *J. Am. Soc. Mass Spectrom.* **1996**, *7*, 1151.
(33) Yin, W. W.; Marshall, A. G.; Marcalo, J.; de Matos, A. P. *J. Am. Chem. Soc.* **1994**, *116*, 8666.
(34) Carretas, J. M.; de Matos, A. P.; Marcalo, J.; Pissavini, M.; Decouzon, M.; Geribaldi, S. *J. Am. Soc. Mass Spectrom*. **1998**, *9*, 1035.
(35) Marchande, N.; Breton, S.; Geribaldi, S.; Carretas, J. M.; De Matos, A. P.; Marcalo, J. *Int. J. Mass Spectrom.* **2000**, *195/196*, 139.
(36) Vieira, M. D.; Marcalo, J.; de Matos, A. P. *J. Organomet. Chem*. **2001**, *632*, 126.
(37) Koyanagi, G. K.; Zhao, X.; Blagojevic, V.; Jarvis, M. J. Y.; Bohme, D. K. *Int. J. Mass Spectrom*. **2005**, *241*, 189.
(38) Zhao, X.; Koyanagi, G. K.; Bohme, D. K. *Can. J. Chem*. **2005**, *83*, 1839.
(39) Cheng, P.; Koyanagi, G. K.; Bohme, D. K. Manuscript in preparation.
(40) Koyanagi, G. K.; Lavrov, V. V.; Baranov, V.; Bandura, D.; Tanner, S.; McLaren, J. W.; Bohme, D. K. *Int. J. Mass Spectrom.* **2000**, *194*, L1.
(41) Koyanagi, G. K.; Baranov, V. I.; Tanner, S. D.; Bohme, D. K. *J. Anal. Atom. Spectrom.* **2000**, *15*, 1207.

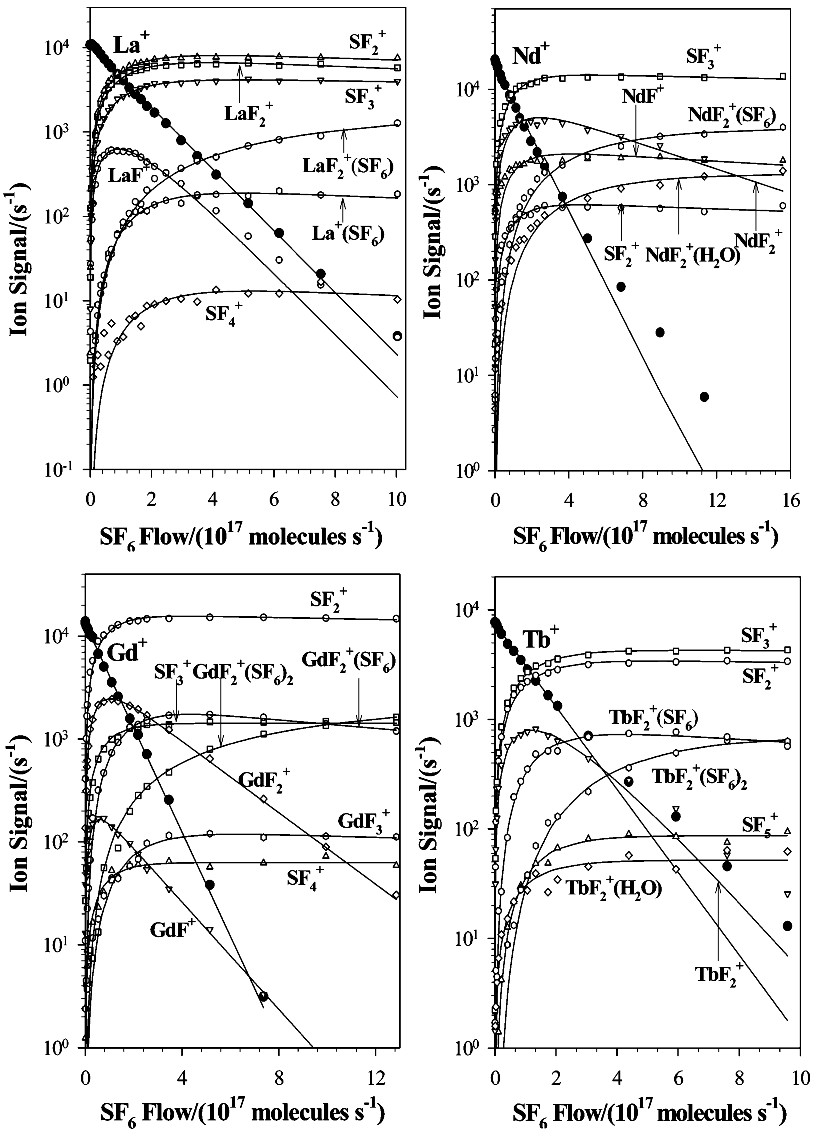


Figure 1. Reactant and product-ion intensities observed for the reactions of La$^+$, Nd$^+$, Gd$^+$, and Tb$^+$ cations with SF$_6$, as a function of SF$_6$ flow. The solid lines represent a fit of the experimental data points with the solutions of the differential equations for the observed reactions.

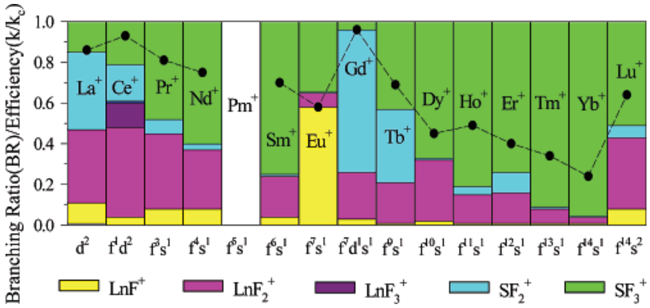


Figure 2. Periodic variation in the reaction efficiency, k/k_c (represented as solid circles), and product distribution for reactions of 14 atomic Ln$^+$ cations with SF$_6$ under ICP−SIFT conditions. The reaction of the Pm$^+$ cation was not investigated.

developed by Su and Chesnavich[42] with $\alpha(SF_6) = 6.54 \times 10^{-24}$ cm^3.[43] Figure 2 displays the data in Table 1 and shows the trends in overall reaction efficiency and product distributions across the lanthanide series.

The primary reactions are fast and exhibit rate coefficients in the range from 1.6×10^{-10} (Yb$^+$) to 6.6×10^{-10} (Gd$^+$) cm^3 molecule^{-1} s^{-1}. Two types of product channels predominate, and these are indicated in reaction 1.

$$Ln^+ + SF_6 \rightarrow LnF_n^{\ +} + SF_{6-n} \qquad (\text{for } n = 1, 2, 3) \qquad (1a)$$

$$\rightarrow LnF_{6-n} + SF_n^{\ +} \qquad (\text{for } n = 1, 2, 3) \qquad (1b)$$

Channel 1a can be described as single or multiple F atom transfer, whereas channel 1b formally corresponds to single or multiple F atom transfer accompanied by electron transfer upon product separation. SF$_6$ addition also was observed with some cations (La$^+$, Ce$^+$, and Pr$^+$) but at levels of <1%. As expected from the much lower first ionization energy of the lanthanides, IE(Ln), all <6.3 eV, compared to IE(SF$_6$) = 15.7 eV,[44] electron transfer was not observed for any of the Ln$^+$ cations. Often multiple channels were observed with a

---

[42] Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

[43] Lide, D. R. *CRC Handbook of Chemistry and Physics*, 80th Edition; CRC Press: Boca Raton, FL, 2001.

[44] Bieri, G.; Aasbrink, L.; Von Niessen, W. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *27*, 129.

Table 1. Primary Reaction Rate Coefficients and Calculated Collision Rate Coefficients, Reaction Efficiencies, Primary Product Distribution, and Higher-Order Product Ions Measured for Reactions of Atomic Ln^+ Cations with SF_6 in Helium at 0.35 ± 0.01 Torr and 295 ± 2 K

Ln^+ cation	k^a (10^{-10} cm^3 molecule^{-1} s^{-1})	$k_c{}^b$ (10^{-10} cm^3 molecule^{-1} s^{-1})	reaction efficiency, k/k_c	primary products	product distribution, PD^c (%)	higher-order product ions^d
La^+	6.1	7.10	0.86	LaF^+	10	$LaF_2{}^+(SF_6)$
				$LaF_2{}^+$	36	
				$SF_2{}^+$	38	
				$SF_3{}^+$	15	
				$La^+(SF_6)$	1	
Ce^+	6.6	7.08	0.93	CeF^+	4	$CeF_2{}^+(SF_6)$
				$CeF_2{}^+$	44	$CeF_3{}^+(SF_6)$
				$CeF_3{}^+$	12	
				SF^+	1	
				$SF_2{}^+$	18	
				$SF_3{}^+$	21	
Pr^+	5.7	7.07	0.81	PrF^+	8	$PrF_2{}^+(SF_6)$
				$PrF_2{}^+$	37	
				$SF_2{}^+$	7	
				$SF_3{}^+$	47	
				$Pr^+(SF_6)$	1	
Nd^+	5.3	7.03	0.75	NdF^+	8	$NdF_2{}^+(SF_6)$
				$NdF_2{}^+$	29	
				$SF_2{}^+$	3	
				$SF_3{}^+$	60	
Sm^+	4.5	6.96	0.70	SmF^+	4	$SmF_2{}^+(SF_6)_{1-2}$
				$SmF_2{}^+$	20	
				$SF_2{}^+$	1	
				$SF_3{}^+$	75	
Eu^+	4.0	6.94	0.58	EuF^+	58	$EuF_2{}^+(SF_6)$
				$EuF_2{}^+$	7	
				$SF_3{}^+$	35	
Gd^+	6.6	6.88	0.96	GdF^+	3	$GdF_2{}^+(SF_6)_{1-2,}$
				$GdF_2{}^+$	23	
				$SF_2{}^+$	70	
				$SF_3{}^+$	4	
Tb^+	4.7	6.86	0.69	TbF^+	1	$TbF_2{}^+(SF_6)_{1-2}$
				$TbF_2{}^+$	21	
				$SF_2{}^+$	34	
				$SF_3{}^+$	43	
				$SF_5{}^+$	1	
Dy^+	3.1	6.82	0.45	DyF^+	4	$DyF_2{}^+(SF_6)_{1-2}$
				$DyF_2{}^+$	16	
				$SF_2{}^+$	2	
				$SF_3{}^+$	78	
Ho^+	3.5	6.80	0.49	HoF^+	1	$HoF_2{}^+(SF_6)_{1-2}$
				$HoF_2{}^+$	14	
				$SF_2{}^+$	4	
				$SF_3{}^+$	81	
Er^+	3.1	6.79	0.40	ErF^+	1	$ErF_2{}^+(SF_6)_{1-2}$
				$ErF_2{}^+$	15	
				$SF_2{}^+$	10	
				$SF_3{}^+$	74	
Tm^+	2.3	6.77	0.34	TmF^+	1	$TmF_2{}^+(SF_6)_{1-2}$
				$TmF_2{}^+$	7	
				$SF_2{}^+$	1	
				$SF_3{}^+$	91	
Yb^+	1.6	6.73	0.24	YbF^+	1	$YbF_2{}^+(SF_6)_{1-2}$
				$YbF_2{}^+$	3	
				$SF_3{}^+$	96	
Lu^+	4.3	6.71	0.64	LuF^+	8	$LuF_2{}^+(SF_6)_{1-2}$
				$LuF_2{}^+$	35	
				$SF_2{}^+$	6	
				$SF_3{}^+$	51	

[a] Measured reaction rate coefficient with an estimated accuracy of ±30%. [b] Calculated capture rate coefficient (see text). [c] Product distribution expressed as a percentage, with an estimated accuracy of ±5%. Products with PD < 1% are not included. [d] The higher-order $LnF_n{}^+(SF_6)_{1,2}$ product ions are derivatives of the corresponding $LnF_n{}^+$ product ions of the primary reactions.

particular reactant ion; as many as six different ions were observed as primary products in the reaction with the Ce^+ cation.

Although $SF_n{}^+$ ions showed no further reactivity with SF_6 in the flow range investigated in our experiments, SF_6 addition according to reaction 2 was observed for most $LnF_m{}^+$ ions (the observed product ions are listed in Table 1). These addition reactions are expected to be termolecular, with helium buffer-gas atoms acting as the stabilizing third body.

$$LnF_m{}^+(SF_6)_n + SF_6 \rightarrow LnF_m{}^+(SF_6)_{n+1} \qquad (m = 1\text{-}3) \qquad (2)$$

Table 2. Fluorine Atom Affinities and Selected Electronic Properties for Atomic Lanthanide Cations

Ln^+ cation	fluorine atom affinity, $FA(Ln^+)$[a]	Ln^+ ground-state valence configuration	Ln^+ term symbol	promotion energy to first $5d^16s^1$ configuration[b]
La^+	157.5 174.9[c]	$5d^2$	$^3F_2$	4.5 ± 4.3
Ce^+	146.4 151.2[d]	$4f^15d^2$	$^4H_{7/2}°$	4.6 ±5.7
Pr^+	146.1 138.3[d]	$4f^36s^1$	$(9/2,1/2)_4°$	22.3 ± 0.8
Nd^+	143.8 ± 4.9 143 ± 7[e]	$4f^46s^1$	$^6I_{7/2}$	34.8 ±8.3
Pm^+	143.5	$4f^56s^1$	$^7H_2°$	46.4 ± 7.2
Sm^+	145.0 ± 3.7 130 ± 7[e]	$4f^66s^1$	$^8F_{1/2}$	62.1 ± 5.8
Eu^+	139.5 ± 3.7	$4f^76s^1$	$^9S_4°$	92.8 ± 5.0
Gd^+	140.7 ± 5.7	$4f^75d^16s^1$	$^{10}D_{5/2}°$	0.0
Tb^+	148.4	$4f^96s^1$	$(15/2,1/2)_8°$	9.3 ± 8.1
Dy^+	127.8 ± 5.7 125 ± 7[e]	$4f^{10}6s^1$	$(8,1/2)_{17/2}$	36.0 ± 6.1
Ho^+	122.7 ± 4.9 129.8[f] 127 ± 7[f]	$4f^{11}6s^1$	$(15/2,1/2)_8°$	37.8 ± 5.4
Er^+	131.2 ± 5.7 131 ± 7[f]	$4f^{12}6s^1$	$(6,1/2)_{13/2}$	34.5 ± 3.1
Tm^+	128.4 ± 3.7	$4f^{13}6s^1$	$(7/2,1/2)_4°$	55.5 ± 7.4
Yb^+	133.2 ± 3.4 123.6[d]	$4f^{14}6s^1$	$^2S_{1/2}$	79.4 ± 4.0
Lu^+	90.1	$4f^{14}6s^2$	$^1S_0$	36.6 ± 3.6

[a] From ref 45, unless indicated otherwise. The units are in kcal mol^{-1}. [b] From ref 30. The units are in kcal mol^{-1}. [c] From ref 46. [d] From ref 47. [e] From ref 27. [f] From ref 48.

Up to two sequential additions of SF_6 were observed for $LnF_2^+ = LaF_2^+$, CeF_2^+, PrF_2^+, NdF_2^+, and EuF_2^+ ($n = 0$), for SmF_2^+, GdF_2^+, TbF_2^+, DyF_2^+, HoF_2^+, ErF_2^+, TmF_2^+, YbF_2^+ and LuF_2^+ (for $m = 2$, $n = 0, 1$), and for $LnF_3^+ = CeF_3^+$ (for $n = 0$). In a few cases, higher-order product ions of the type $LnF_2^+(SF_6)$ were observed to react with the water impurity through ligand exchange reactions of the type (3). This is manifested in Figure 1 by the rise in $NdF_2^+(H_2O)$ and $TbF_2^+(H_2O)$.

$$LnF_2^+(SF_6) + H_2O \rightarrow LnF_2^+(H_2O) + SF_6 \tag{3}$$

3.1. Periodicity in Reaction Efficiency. The room-temperature efficiencies of the primary reactions of 14 Ln^+ cations with SF_6 are presented in Table 1 and range from 0.24 (Yb^+) to 0.96 (Gd^+). The reaction efficiencies with La^+ ($5d^2$), Ce^+ ($4f^15d^2$) and Gd^+ ($4f^75d^16s^1$) are the highest among all 14 reactions (close to 100%), and it is interesting to note that these cations all have two non-f electrons in their electronic ground state. The efficiencies of the reactions with the early lanthanide cations (La^+ to Eu^+) show a systematic decrease from 0.86 to 0.58 and those with the late transition-metal cations (Gd^+ to Yb^+) from 0.96 to 0.24. The Lu^+ cation is unique in its electronic configuration ($4f^{14}5s^2$) and reactivity (0.64). An overview of the periodicity in reaction efficiency across the entire lanthanide series is included in Figure 2.

3.2. Trends in Product Formation. The observed product channels in the primary chemistry of the Ln^+ cation with SF_6 are many, and the variation in their relative importance across the lanthanide row is most intriguing. The observed channels are dominated by the abstraction of multiple F atoms, apparently without or with ensuing fluoride transfer upon product separation, and result in the generation of ionized metal fluorides (LnF_n^+) by reaction 1a or partially defluorinated SF_6 cations (SF_n^+) by reaction 1b.

Formation of LnF^+ (+ SF_5) by F-atom transfer was observed with all the lanthanide cations, but never as a major product ion (≤10%), except with Eu^+ (f^7s^1) for which 58% of the reactive collisions involve F-atom transfer. The known F-atom affinity (*FA*) of the lanthanide cations that is summarized in Table 2 indicate that F-atom transfer from SF_6 is exothermic with all the Ln^+ ions investigated except perhaps Lu^+: $FA(Ln^+) \geq 123$ kcal mol^{-1} for all the atomic lanthanide cations (except Lu^+) and $FA(SF_5) = 93.6 \pm 0.1$ kcal mol^{-1}. Table 3 indicates that F-atom transfer is exothermic by more than 29 and as much as 64 kcal mol^{-1} for all lanthanide cations except Lu^+, for which it is essentially thermoneutral. The production of LnF^+ and LnF_2^+ in the reactions of Tb^+ and Ho^+ with SF_6 has been reported previously by Gibson.[18]

LnF_2^+ (+ SF_4) is the predominant LnF_n^+ product ion that was observed, except with the Eu^+ cation. Table 3 indicates that the formation of $LnF_2^+ + SF_4$ is exothermic by more than 76 kcal mol^{-1} and even the formation of $LnF_2^+ + SF_3 + F$ is exothermic by at least 5 kcal mol^{-1} (except for Lu^+). Figure 2 shows a general decrease in the importance of the LnF_2^+ channel along the lanthanide row, with the reactions of Eu^+ and Lu^+ as exceptions.

---

(45) Kaledin, L. A.; Heaven, M. C.; Field, R. W. *J. Mol. Spectrosc.* **1999**, *193*, 285.

(46) Zhang, D. J.; Zhang, C. Q.; Liu, C. B. *J. Organomet. Chem.* **2001**, *640*, 121.

(47) Zhang, D.; Liu, C.; Bi, S. *J. Phys. Chem. A* **2002**, *106*, 4153.

(48) Gibson, J. K. *J. Fluor. Chem.* **1996**, *78*, 65.

Table 3. Overall Changes in Enthalpy for the Formation of Various Products in the Reaction of the Ln^+ Cation with SF_6

	Change in Enthalpy, $-\Delta H°$ (kcal mol^{-1})				
M^+ cation	$LnF^+ + SF_5$[a]	$LnF_2^+ + SF_4$[b]	$LnF_2^+ + SF_3 + F$[b]	$LnF_3 + SF_3^+$[c]	$LnF_3 + SF_2^+ + F$[c]
La^+	63.9	127	46	153	60
Ce^+	52.8	132	51	139	46
Pr^+	52.5	114	33	127	35
Nd^+	50.2	102	21	120	28
Pm^+	49.9	104	23	120	27
Sm^+	51.4	106	25	117	24
Eu^+	45.9	100	19	102	10
Gd^+	47.1	127	46	143	50
Tb^+	54.8	125	44	139	46
Dy^+	34.2	91	10	104	12
Ho^+	29.1	86	5	102	9
Er^+	37.6	101	20	117	24
Tm^+	35.8	92	11	108	16
Yb^+	39.6	96	15	112	19
Lu^+	−3.5	76	−5	92	−1

[a] Calculated based on the bond dissociation energy BDE(Ln^+-F) from ref 45 and $\Delta H_f°(SF_n)$, $\Delta H_f°(F)$ from ref 16. [b] Calculated based on the BDE(Ln^+-F), ionization energy IE(LnF) from ref 45, IE(LnF_2) and BDE(LnF_2) from ref 49, and $\Delta H_f°(SF_n)$ and $\Delta H_f°(F)$ from ref 16. [c] Calculated based on the BDE(Ln^+-F), IE(LnF) from ref 45, IE(LnF_2) and BDE(LnF_2), BDE(LnF_3) from ref 49, and $\Delta H_f°(SF_n)$, $\Delta H_f°(SF_n^+)$, and $\Delta H_f°(F)$ from ref 16.

LnF_3^+ is observed only with the very reactive Ce^+ (f^1d^2) cation and no LnF_4^+ ions were observed as products.

SF_2^+ and SF_3^+ are the predominant SF_n^+ product ions that were observed. Table 3 indicates that formation of $SF_3^+ + LnF_3$ is very exothermic, by more than 92 kcal mol^{-1}, and that even the formation of $SF_2^+ + F + LnF_3$ is exothermic by more than 9 kcal mol^{-1} (except for Lu^+). Both of these channels leave the Ln in its maximum valence state. The formation of SF_2^+ *decreases* in importance along the early and late lanthanides and predominates only very early with La^+ (d^2) and with Gd^+ ($f^7d^1s^1$). In contrast, the formation of SF_3^+ (+ LnF_3) increases in importance along the early and late lanthanides and predominates beyond the La^+ and Gd^+ cations, with the reactions of the Eu^+ and Lu^+ cations again being exceptions.

Trace amounts of the SF^+ cation were observed only with Ce^+ and no SF_4^+ ions were observed as products.

3.3. Correlation of Reaction Efficiency with Promotion Energy. Our experimental results indicate that Gd^+ ($4f^75d^16s^1$) with two nonf valence electrons in its ground electronic state exhibits the highest reaction efficiency, followed closely by Ce^+ ($5d^2$) and La^+ ($4f^15d^2$), which also have two non-f valence electrons available for bonding. The reactivities of the remaining Ln^+ cations (excluding Lu^+), all of which have available only one non-f electron (s^1) in their ground states, are all less and decrease along the early and late lanthanide series. Therefore, apparently, the s electron, at most, plays a small role in determining these latter reactivities. Indeed, previous experience by others[22] and our own experience with O-atom transfer reactions[30] indicate that the efficiency of these reactions is governed by the promotion of an f electron in the Ln^+ cation, which makes two electrons available for bonding. A similar correlation is observed here for reactions of Ln^+ cations with SF_6.

Figure 3 shows that the periodicity in the efficiency of the measured reactions of Ln^+ cations with SF_6 follows the variation across the lanthanide row in the energy required to promote an f electron to achieve a $5d^16s^1$ configuration. Such a promotion would make two electrons available for bonding with two F atoms to produce LnF_2^+. Promotion to a $5d^2$ configuration, which makes available two unpaired 5d valence electrons rather than a 5d and a 6s electron,[50] would achieve the same result and the variation in electron promotion energy across the lanthanide row would be similar. Lu^+ ($f^{14}s^2$) should be regarded as an exception to the lanthanide cation series in that a 6s electron rather than a 4f electron would be promoted to achieve a d^1s^1 configuration.

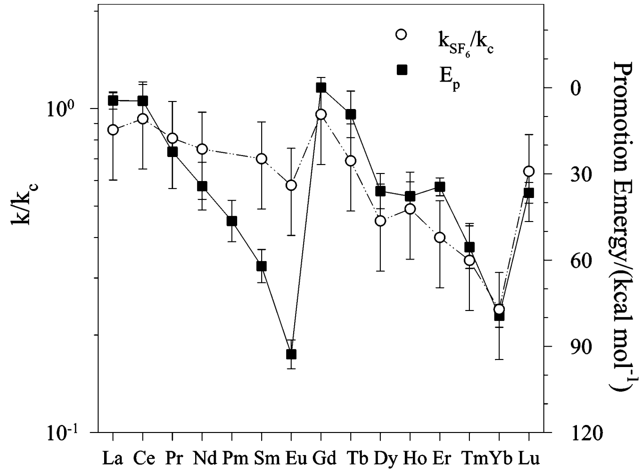


Figure 3. Reaction efficiency (open circles and left ordinate axis) and the energy required to achieve a Ln^+ (d^1s^1) configuration by electron promotion (solid squares and right ordinate axis) plotted along the lanthanide row of elements for reactions with SF_6. There is an apparent correlation between reaction efficiency and electron-promotion energy.

The semilogarithmic plot in Figure 4 shows an Arrhenius-like dependence of the reaction efficiency (k/k_c) at room temperature on the electron promotion energy of Ln^+ (E_p), similar to that which we have observed previously with atom-transfer reactions with other molecules (such as N_2O, CH_3F,

---

(49) Zmbov, K. F.; Margrave, J. L. In *Mass Spectrometry in Organic Chemistry*; Gould, R. F., Ed.; Advances in Chemistry, Series No. 72; American Chemical Society: Washington, DC, 1968; p 267.

(50) Gibson, J. K. *J. Phys. Chem. A* **2003**, *107*, 7891.

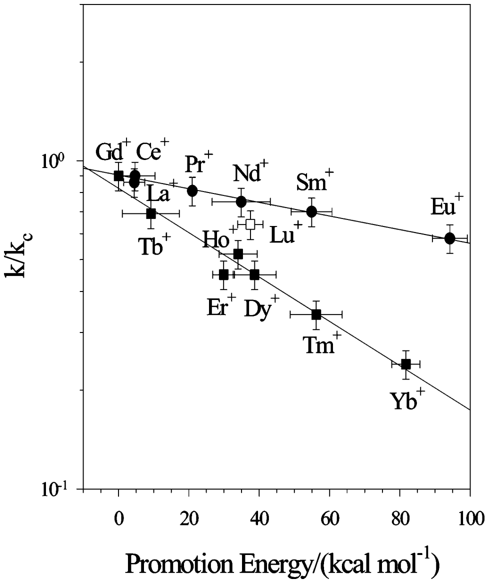


Figure 4. Arrhenius-like correlation of reaction efficiency with the energy required to promote an electron and leave the Ln^+ ion in a d^1s^1 configuration in the reaction of early (solid circles) and late (solid squares) Ln^+ ions with SF_6. Lu^+ (open square) is an exception to the trend observed for the late Ln^+ ions. The vertical bars represent the estimated relative uncertainty of the rate coefficient measurements (±10%).

CH_3Cl, and D_2O).[51] The exponential dependence is described by eq 4:

$$\frac{k}{k_c} = \exp\left(-XE_p\right) \quad (4)$$

Here, reactivity is expressed as reaction efficiency. The early and late lanthanides define different lines with different slopes (with Lu^+ as an exception). If X is interpreted as $1/RT_{eff}$, the slopes of the semilogarithmic plots indicate effective temperatures of 45 500 and 14 000 K, or RT_{eff} = 3.9 and 1.2 eV, for the early and late Ln^+ ions, respectively. We have seen such differences in effective temperature previously and ascribed them to differences in promotion efficiency: electron promotion in the early lanthanide cations involves an unpaired f electron, whereas that in the late Ln^+ ions involves a paired electron and, therefore, electron−electron repulsion.

3.4. A Note on Reaction Mechanism. The periodicity in the measured reaction efficiency for the reactions of the Ln^+ cation with SF_6 reactivity (see Section 3.3) indicates that, as a first step, two valence electrons are made available in the Ln^+ cation during the formation of an intermediate complex of $[Ln{-}SF_6]^{+*}$. This requires electron promotion to achieve either a d^1s^1 or a d^2 excited electronic configuration in the Ln^+ cation. Product formation would then be determined by intramolecular S−F bond activation interactions of the type shown in reaction 5 within the intermediate complex $[Ln\text{-}SF_6]^{+*}$ during its lifetime. Detailed potential energy surfaces are not available to provide a proper analysis of reaction dynamics; however, we can at least assess the role of overall reaction thermodynamics and the electronic configuration of Ln^+ from a further inspection of the measured product distributions.

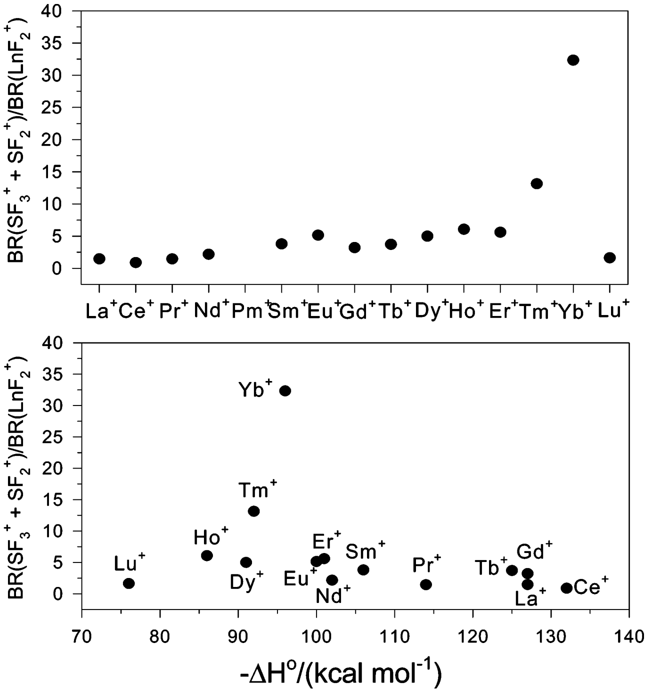
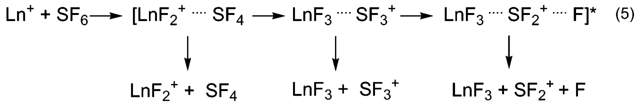


Figure 5. Correlation of the ratio of the sum of branching ratios for $SF_{2,3}^+$ formation to the branching ratio for LnF_2^+ formation in reactions of Ln^+ with SF_6 with the electronic configuration of Ln^+ (top) and the exothermicity for the formation of LnF_2^+ + SF_4.



The moderately exothermic formation of LnF^+ is always a minor channel, except with Eu^+. Table 3 shows that the concomitant transfer of two F atoms to Ln^+ is much more exothermic than the transfer of one F atom, usually by more than 50 kcal mol^{-1} (the difference is 79 kcal mol^{-1} for the reaction with Ce^+). Except for the reaction with Lu^+, for which the formation of SF_3^+ is observed to be comparatively less favorable, the formation of SF_3^+ + LnF_3 is slightly more exothermic overall than the formation of LnF_2^+ + SF_4 (by 2−26 kcal mol^{-1}; see Table 3) and this would favor the transfer of a F^- anion from SF_4 to LnF_2^+ to form SF_3^+ prior to the separation of products. Indeed, this transfer is sufficiently exothermic to be accompanied by the elimination of a F atom from SF_3^+ and concomitant formation of SF_2^+; this latter channel becomes increasingly more favorable as it becomes more exothermic.

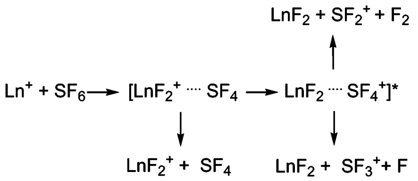
Figure 5 explores the variation in the extent of F^- anion transfer with the electronic configuration of Ln^+ and the exothermicity for the formation of LnF_2^+ + SF_4. $SF_{2,3}^+$ formation, presumably as a consequence of intramolecular fluoride transfer, is observed to be preferred in a periodic manner, and this is dramatically so for the final two members, Tm^+ and Yb^+, of the late lanthanide cations. The weak correlation with exothermicity shown in Figure 5 suggests that electronic effects predominate over the thermodynamic

---

(51) Cheng, P.; Koyanagi, G. K.; Bohme, D. K. *ChemPhysChem*. **2006**, *7*, 1813.

influence in determining the relative importance of fluoride transfer within the intermediate complex before it separates.

An alternative—and, perhaps, intuitively more plausible—mechanism involves electron transfer or dissociative electron transfer between the products before they separate, as indicated in reaction 6.



(6)

The product distribution would then be governed by the relative ionization energy of LnF_2 and SF_4 and the exothermicity available for internal excitation. However, known ionization energies[15,49] for LnF_2 and SF_4 indicate that dissociative electron transfer from SF_4 to LnF_2^+ to produce SF_3^+ (+ F) is endothermic for at least 13 of the 15 lanthanides investigated.

4. Conclusions

Lanthanide cations react with SF_6 at room temperature mainly by multiple rather than by single F-atom abstraction. The gas-phase reactions are all very fast, with reaction efficiencies in the range of 0.24−0.96. The primary products are LnF_n^+ and SF_n^+ (where $n = 1-3$), with $n = 2$ for LnF_n^+ and $n = 3$ for SF_n^+ accounting for most of the product ions. The efficiencies of reaction and the distributions of the primary products LnF^+, LnF_2^+, SF_3^+, and SF_2^+ correlate with the electron promotion energy required to achieve two valence electrons in the Ln^+ cation. The reaction efficiency decreases as the electron promotion energy increases, and the observed periodicity in reaction efficiency along the lanthanide series matches the periodic trend in the corresponding electron promotion energy. A remarkable Arrhenius-like correlation is observed for the dependence of reactivity on promotion energy, with the early and late lanthanide cations exhibiting characteristic temperatures of 45 500 and 14 000 K, respectively.

Some of the LnF_n^+ species react further with SF_6 via SF_6 addition (up to 2 additions) under the experimental operating conditions of the ICP/SIFT tandem mass spectrometer.

Acknowledgment. Continued financial support from the Natural Sciences and Engineering Research Council of Canada is greatly appreciated. Also, we acknowledge support from the National Research Council, the Natural Science and Engineering Research Council, and MDS SCIEX in the form of a Research Partnership grant. As holder of a Canada Research Chair in Physical Chemistry, D. K. B. thanks the contributions of the Canada Research Chair Program to this research.

IC061000O