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Gas-Phase Reactions of Transition-Metal Ions with Hexafluorobenzene: Room-Temperature Kinetics and Periodicities in Reactivity

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An inductively coupled plasma (ICP) selected-ion flow tube tandem mass spectrometer has been employed in a systematic survey of room-temperature reactions of C_6F_6 with 29 transition-metal ions. The atomic ions were produced at ca. 5500 K in an ICP source and were allowed to decay radiatively and to thermalize by collisions with Ar and He atoms prior to reaction, although for some atomic ions, this quenching may be incomplete. Rate coefficients and product distributions were measured for the reactions of first-row atomic ions from Sc^+ to Zn^+, of second-row atomic ions from Y^+ to Cd^+ (excluding Tc^+), and of third-row atomic ions from La^+ to Hg^+. Marked differences were observed for reactivities of early and late transition metal cations with regard to both the reaction efficiency and the type of reaction pathway. Remarkable multiple (up to four) fluorine atom abstraction, proceeding close to the collision rate, dominated the chemistry observed with early transition metal cations while simple association of up to two molecules of C_6F_6 to the metal cation dominated the chemistry of late transition metal cations. Correlations were found between the electronic configuration of the metal cation and the nature of the reaction path and the reaction efficiency. Only the early third-row Hf^+, Ta^+, and W^+ transition-metal ions exhibited some C−C and C−F bond-dissociation channels leading to ring cleavage.

Introduction

Fluorocarbons have found many applications in industry, primarily due to their thermal and chemical stability.[1] Although perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs) have replaced the powerful ozone-depleting chlorofluorocarbons (CFCs), an increase in the use of fluorocarbons in general (greenhouse gases) is nowadays controlled since they contribute to global warming. Hence, a need for the chemical conversion of fluorocarbons to less greenhouse active molecules is acute but is a difficult task, due to the special stability of fluorinated compounds.

The stability of fluorinated compounds is rendered by the strength of the C−F bond, usually >110 kcal mol^{-1}.[2] Experiments have shown that metal complexes are unique tools in the activation of the C−F bond under mild conditions in the solution phase.[3] C−F bond activation also has been achieved in reactions occurring on surfaces important in materials science and in the gas phase; the latter provide information about intrinsic features of C−F bond activation in the absence of solvent molecules, ligands, or counterions.[4−10] Mazurek and Schwarz have reviewed both of these chemistries very recently; transition-metal and lanthanide cations are featured as effective activators of fluorinated saturated and unsaturated hydrocarbons in the gas phase.[2] Other gas-phase studies previously have provided results for reactions of some transition-metal cations with SF_6, another powerful greenhouse gas.[10] Multiple fluorine atom abstraction was observed in reactions of early transition metal cations (groups 3−5) with SF_6.[10] Multiple C−F bond activation has also been reported previously; FT-ICR mass spectrometer experiments[4] have demonstrated the 2-fold bond activation of fluorinated ethanes and C_6F_6 by Pr^+ and very recent experiments in our laboratory using inductively coupled plasma selected-ion flow tube (ICP-SIFT) tandem mass spectrometry have demonstrated a most remarkable 4-fold C−F bond activation resulting in the abstraction of four fluorine atoms from C_6F_6 by Nb^+ in one step.[11]

Here we investigate the gas-phase reactivity of all transition-metal cations (except the radioactive Tc^+) toward C_6F_6 using ICP-SIFT tandem mass spectrometry. This is the first systematic study of the reactivity of all the transition-metal cations with a particular fluorocarbon molecule.

Experimental Section

The experiments were performed with the newly configured ICP/SIFT tandem mass spectrometer.[12a−c] The atomic ions were generated in an argon plasma at 5500 K fed with a vaporized solution containing the metal salt. The ions produced were injected through a differentially pumped sampling interface into a quadrupole mass spectrometer and, after mass analysis, introduced through an aspirator-like interface into flowing helium carrier gas at 0.35 Torr and 295 ± 2 K. After experiencing about 10^5 collisions with He atoms, the ions were allowed to react with added C_6F_6. The atomic ions emerging from the atmospheric-pressure plasma have a Boltzmann internal energy distribution characteristic of the plasma temperature.[13] Calculations have indicated that excited states contribute 20% or less toward the populations of Cr^+, Mn^+, Ni^+, Cu^+, Zn^+, Rh^+, Pd^+, Ag^+, Cd^+ Re^+, Au^+, and Hg^+ and 50% or more toward the populations of Ti^+, Y^+, Zr^+, Nb^+, La^+, and Ir^+ with Sc^+, V^+, Fe^+, Co^+, Mo^+, Ru^+, Hf^+, Ta^+, W^+, and Pt^+ having intermediate distributions with Os^+ not known.[13] However, these populations are expected to be downgraded during sampling

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TABLE 1: Measured Rate Coefficients for Primary Reactions of Transition-Metal Cations with C_6F_6 (k in units of cm^3 $molecule^{-1}$ s^{-1}), Reaction Efficiencies (k/k_c) k_c = Calculated Collision Rate Coefficients (see text), and Branching Ratios (BRs) for Observed Primary Product Ions[a]

M	$k/10^{-10}$	k/k_c	$C_6F_6^+$	$MC_6F_6^+$	MF^+	MF_2^+	MF_3^+	MF_4^+	$C_6F_2^+$	$C_6F_3^+$	$C_6F_4^+$	$C_2F_3^+$	$C_2F_4^+$	$C_3F_3^+$
Sc	12	1.0			0.12	0.57	0.050			0.26				
Y	9.3	1.0			0.050	0.95								
La	8.1	1.0			0.30	0.70								
Ti	12	1.0				0.13	0.050		0.62	0.20				
Zr	9.3	1.0				0.10	0.15		0.75					
Hf	7.6	1.0				0.030	0.030		0.87	0.010	0.010	0.010	0.040	
V	8.9	0.77		0.55		0.30				0.15				
Nb	8.6	0.93		0.0050			0.015	0.965		0.015				
Ta	7.6	1.0			0.0030	0.0030	0.015	0.60	0.019	0.175	0.0050	0.0050		0.175
Cr	2.5	0.23		0.95	0.050									
Mo	2.7	0.29		1.0										
W	7.6	1.0		0.10				0.20	0.60	0.010	0.060			0.030
Mn	≥0.32	≥0.029		0.90	0.10									
Re	≥0.27	≥0.035		1.0										
Fe	6.5	0.59		0.95	0.050									
Ru	8.9	1.0		1.0										
Os	7.5	1.0		1.0										
Co	8.7	0.81		1.0										
Rh	8.9	1.0		1.0										
Ir	6.7	0.90		1.0										
Ni	10	0.94		0.85	0.15									
Pd	7.3	0.82		0.90	0.10									
Pt	6.9	0.93		1.0										
Cu	9.9	0.94		0.95	0.050									
Ag	≥2.0	≥0.23		0.90	0.10									
Au	7.4	1.0	0.06	0.94										
Zn	3.5	0.34		0.90	0.10									
Cd	≥0.084	≥0.0098		0.50	0.50									
Hg	7.4	1.0	1.0											

[a] Uncertainties in k are estimated to be ±30% and BRs are rounded off to the nearest 5 in the third digit.

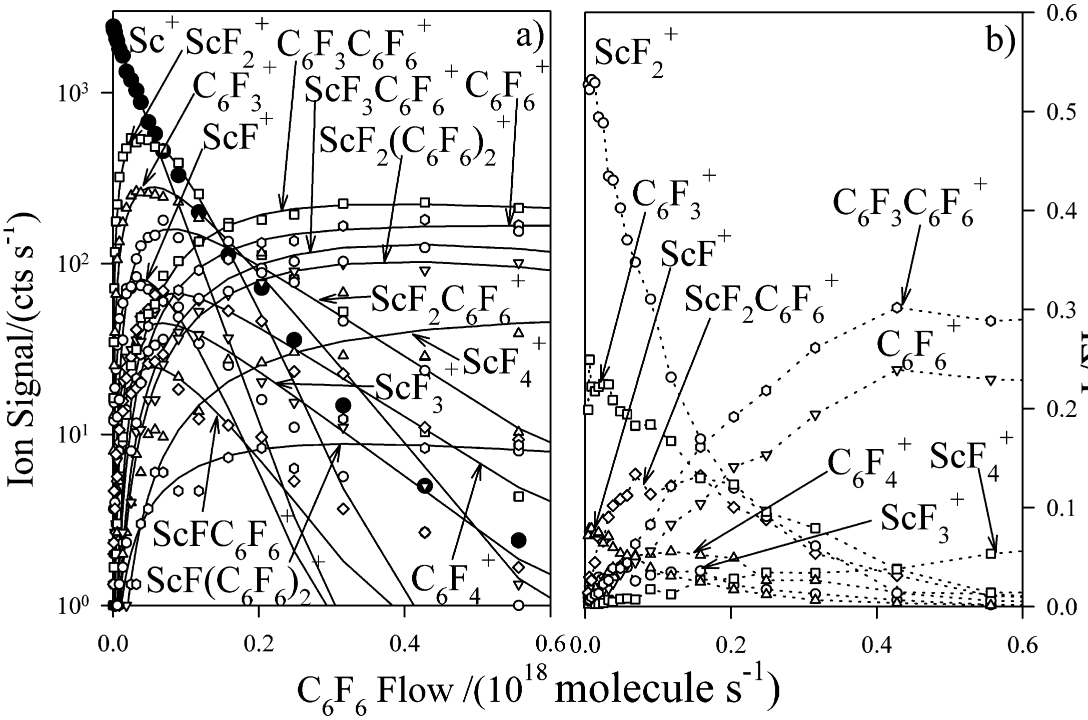

Figure 1. (a) Reactant and product-ion intensities observed for the reactions of Sc^+ with C_6F_6 as a function of C_6F_6 flow. The solid lines represent a fit of the experimental data points with the solutions of the differential equations appropriate for the observed reactions. (b) Plot of fractional abundance of ionized products as a function of the C_6F_6 flow. The zero-flow intercepts provide the branching ratios (BRs) for the primary reaction products listed in Table 1.

toward a thermal-energy distribution by collisions with argon atoms and by radiative decay as well as by the 10^5 collisions with He before entry into the reaction region. The extent to which quenching of electronically excited states is complete is uncertain and could be inferred only indirectly from the observed decays of primary ion signals and observed product ions, but collisions with Ar and He 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 still further downstream with a second quadrupole mass spectrometer and were measured as a function of added reactant. The resulting profiles

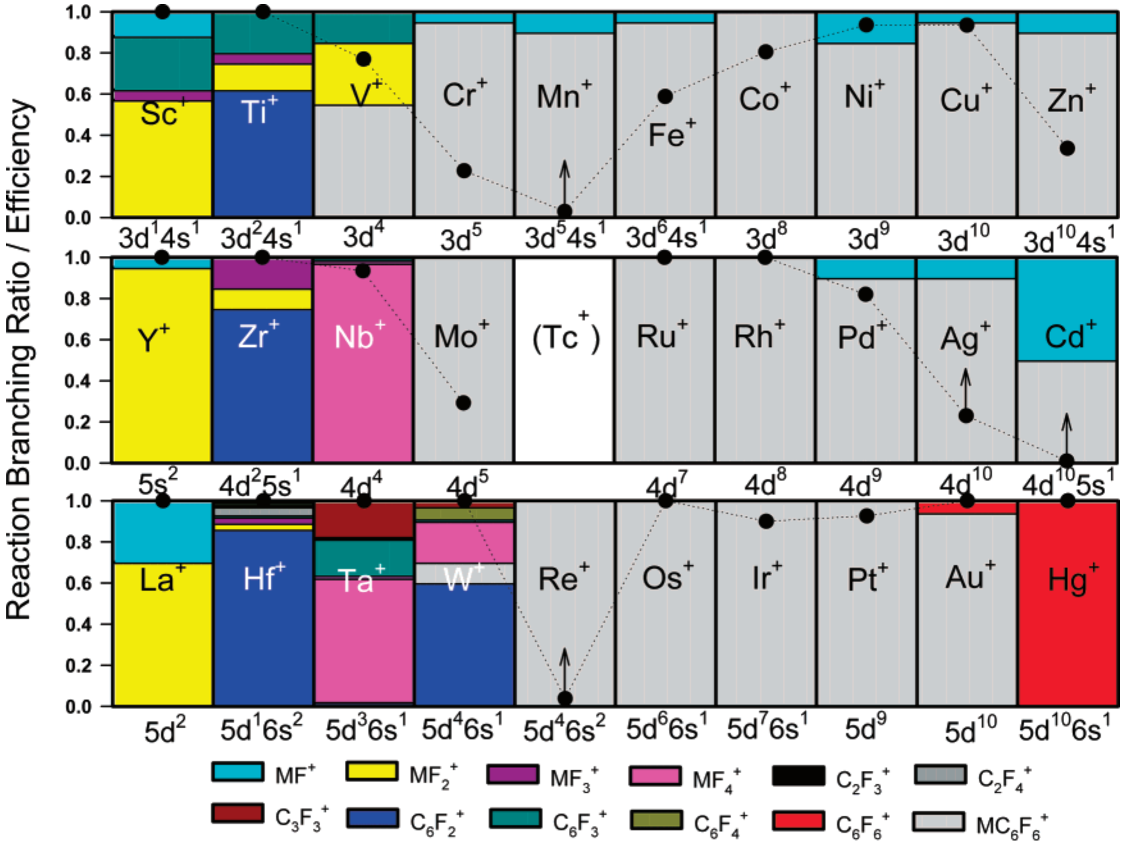

Figure 2. Results for primary reactions of transition-metal cations with C_6F_6 under ICP-SIFT conditions. BRs for competing primary reaction channels are represented on a bar graph with color-coded reaction channels. Also represented as solid symbols are reaction efficiencies defined as the ratio of measured rate coefficient k and the collision rate coefficient k_c calculated using the variational transition state theory.[15]

provide information about product-ion distributions, reaction rate coefficients, and reaction molecularity. Rate coefficients for the primary reactions of all ions are determined from the rate of decay of the reactant ion intensity with an uncertainty estimated to be less than ±30%.[14] Often adduct formation is observed, and this can lead to curvature in the primary-ion decay due to the occurrence of reverse reaction to a greater or lesser extent depending on the strength of the bonding. A linear semilogarithmic decay over at least 1 order of magnitude is required to accurately define the forward reaction rate coefficient. Otherwise the rate coefficient is treated as a lower limit. The approach to equilibrium was monitored with a plot of the ratio of the concentration of the adduct ion over that of the bare metal ion. Linearity in such a plot provides a measure of the standard free energy change, ΔG°_{298}, for the addition reaction.

The neutral reagent C_6F_6 (Sigma, 99.9%) was used without further purification, except for multiple freeze−pump−thaw cycles to remove noncondensable gases.

Results and Discussion

The reactions of 29 different transition-metal ions were investigated with C_6F_6. Both the primary and higher-order chemistries were monitored. Results obtained for the primary reactions are summarized in Table 1. The results include measured rate coefficients and product distributions as well as calculated reaction efficiencies. A typical ion intensity−flow profile is illustrated in Figure 1a for the reaction between Sc^+ and C_6F_6 and the distribution of product ions for the same reaction is presented in Figure 1b. The initial slope of the Sc^+ ion signal decay in Figure 1a provides a measure of the (effective) bimolecular reaction rate coefficient, k. Uncertainties in k are estimated to be ±30%.[14] 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. 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 algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich.[15]

Figure 2 displays the data in Table 1 on a periodic table and shows the trends in overall reaction efficiencies and product distributions across this table for reactions of transition-metal cations with C_6F_6. It is immediately obvious from a quick glance at this table that the early transition metal cations show a much richer chemistry than the late transition metal cations and that there are also periodic features in the reaction efficiency.

Experimental results for the reactions of all first-row transition-metal cations with C_6F_6 are presented in Figure 1 (Sc^+), Figure 3 (Ti^+ and V^+), Figure 4 (Cr^+, Mn^+, Fe^+, and Co^+), and Figure 5 (Ni^+, Cu^+, and Zn^+).

Primary Chemistry

Overview of Primary Chemistry. Six types of primary reactions were observed with C_6F_6. These include what formally can be described as single or multiple F atom transfer, reaction 1; single or multiple F atom transfer accompanied by electron transfer upon product separation, reaction 2; ring cleavage with metal bond formation, reactions 3 and 4; addition, reaction 5; and electron transfer, reaction 6. As many as nine different primary product ions were observed to be formed in one reaction

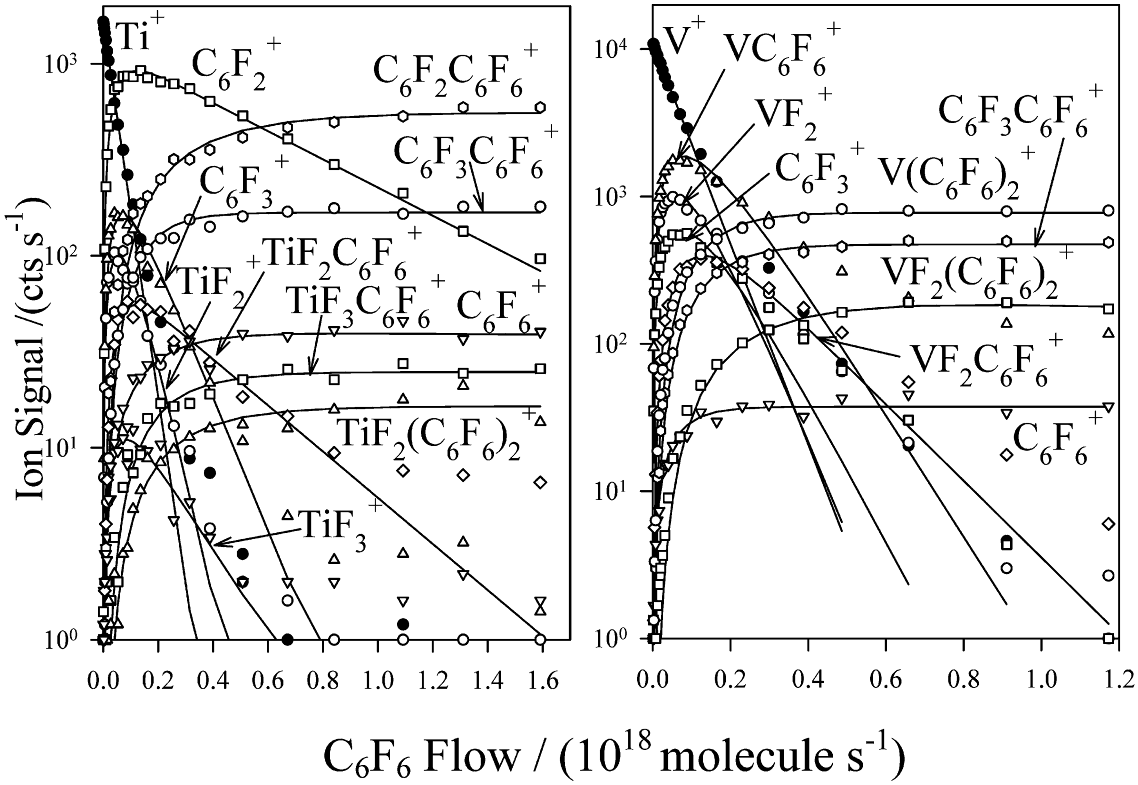

Figure 3. Reactant and product-ion intensities observed for the reactions of Ti^+ and V^+ with C_6F_6 as a function of C_6F_6 flow. The solid lines represent a fit of the experimental data points with the solutions of the differential equations appropriate for the observed reactions.

(with Ta^+)

$$M^+ + C_6F_6 \rightarrow MF_n^{\ +} + C_6F_{6-n} \qquad \text{with } n = 1-4 \qquad (1)$$

$$\rightarrow C_6F_{6-n}^{\ +} + MF_n \qquad \text{with } n = 2-4 \qquad (2)$$

$$\rightarrow C_2F_n^{\ +} + (MC_4F_{6-n}) \qquad \text{with } n = 3,4 \qquad (3)$$

$$\rightarrow C_3F_3^{\ +} + (MC_3F_3) \qquad (4)$$

$$\rightarrow MC_6F_6^{\ +} \qquad (5)$$

$$\rightarrow C_6F_6^{\ +} + M \qquad (6)$$

Trends in Reaction Efficiency. The periodic features in reaction efficiency are as follows. The reaction efficiencies for groups 3−5 transition-metal cations and W^+ are larger than 0.77, with k close or equal to the collision rate coefficient. Groups 6 and 7 transition-metal cations (except W^+) are quite unreactive, with k/k_c lower than 0.29, while group 8−10 transition-metal cations show increased reactivity, with reaction efficiencies higher than 0.59. The cations of first- and second-row groups 11 and 12 transition metals (except Cu^+) exhibit reduced reactivity while third-row Au^+ and Hg^+ reacted at the collision rate. The reduced reactivities of groups 6 and 7 and groups 11 and 12 transition-metal cations can be attributed to weaker bonding interactions perhaps due to the special stability of their half-filled and fully filled valence shells which require the highest amount of energy to reorganize their electronic configurations in order to form covalent bonds.[16] Hg^+ is an exception since it reacts by electron transfer and so does not form a covalent bond.

Trends in Product Formation. The primary chemistry of early transition metal cations with C_6F_6 was dominated by the concerted abstraction of multiple fluorine atoms resulting in generation of the corresponding ionized metal fluorides (reaction 1) or partially de-fluorinated hexafluorobenzene cations (reaction 2). The occurrence of reactions 1 or 2 for a particular metal

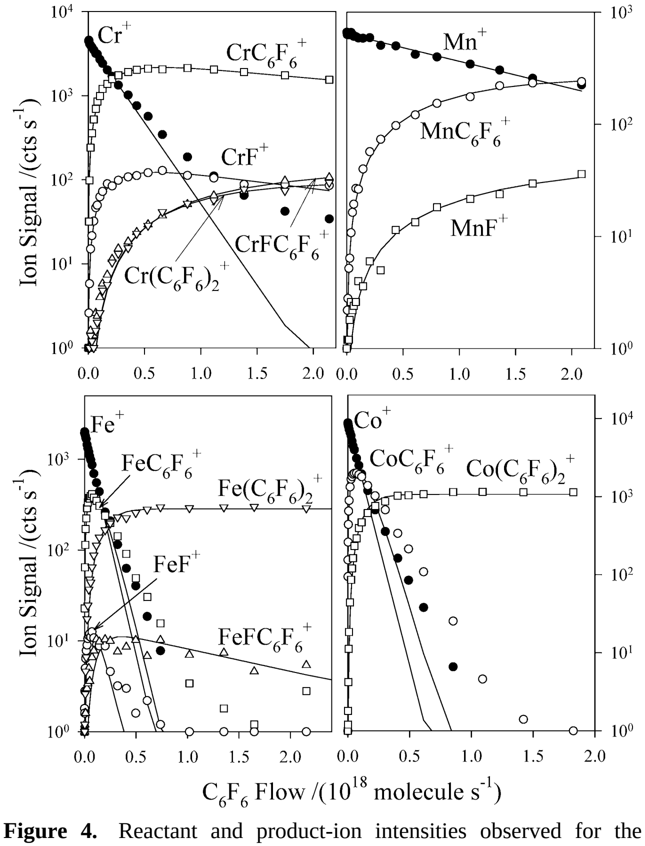

Figure 4. Reactant and product-ion intensities observed for the reactions of Cr^+, Mn^+, Fe^+, and Co^+ with C_6F_6 as a function of C_6F_6 flow. The solid lines represent a fit of the experimental data points with the solutions of the differential equations appropriate for the observed reactions.

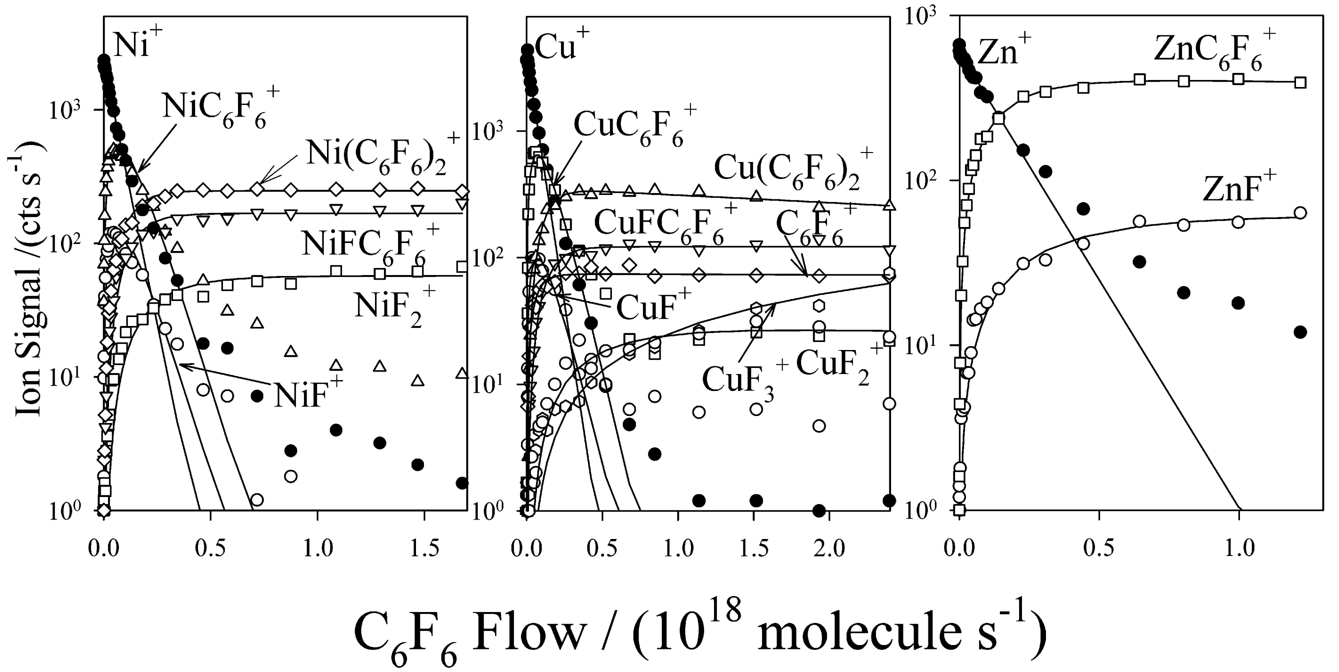

Figure 5. Reactant and product-ion intensities observed for the reactions of Ni^+, Cu^+, and Zn^+ with C_6F_6 as a function of C_6F_6 flow. The solid lines represent a fit of the experimental data points with the solutions of the differential equations appropriate for the observed reactions.

cation depends on the relative ionization energies of the MF_n and C_6F_{6-n} species. However, in some cases, both reactions were observed, indicating small differences in ionization energies of the resulted species. Also, cleavage of the hexafluorobenzene ring according to reactions 3 and 4 was observed to result in the reactions with some early transition metal cations.

The reactions observed with the late transition metal cations usually involve the competition of only two reaction channels, with the simple addition of hexafluorobenzene, reaction 5, the predominant channel. Electron transfer, reaction 6, as well as single fluorine transfer were observed to compete with addition in some cases.

Electron Transfer. Mercury, IE(Hg) = 10.4375 eV,[17] is the only transition metal that has an ionization energy greater than that of hexafluorobenzene, $IE(C_6F_6) = 9.90 \pm 0.04$ eV,[17] so that electron transfer is exothermic at room temperature only for the ground-state reaction of Hg^+ with C_6F_6. Indeed, electron transfer was observed to be the exclusive pathway with Hg^+. There was some indication of the formation of trace amounts (6 ± 2%) of $C_6F_6^+$ in the reaction of Au^+ with C_6F_6, even though this reaction is endothermic by 0.675 eV since IE(Au) = 9.2255 eV.[17] Perhaps there is incomplete thermalization in this case. The population analysis for gold cations at 5500 K (the plasma temperature) indicates that approximately 3% of the Au^+ population would possess enough internal energy to drive the electron-transfer channel. Perhaps the Au^+ cations are even still translationally excited in the reaction region; Au^+ has the largest mass (aside from Hg^+) of the atomic ions investigated.

C_6F_6 Addition. Hexafluorobenzene was observed to attach to some early transition metal cations (V^+ and Nb^+) and to all late transition metal cations except Hg^+. C_6F_6 addition is the predominant reaction channel in the reactions of the late transition metal cations (from group 6 onward), and the efficiency of this channel varies across the periodic table. In the first row, the efficiency is from 0.22 (Cr^+) to a minimum at ≥0.026 (Mn^+) and then rising to 0.90 (Cu^+) and falling to 0.31 (Zn^+). In the second row, the efficiency is 0.29 for Mo^+ (there is no data for Tc^+, which presumably would define the minimum), rises to a maximum of 1.0 for both Ru^+ and Rh^+ and then falls to ≥0.005 for Cd^+. In the third row, Re^+ exhibits the smallest efficiency (≥0.035) which then rises sharply to approximately 1 for Os^+, Ir^+, Pt^+, and Au^+. We attribute these variations to variations in the (generally unknown) bond energy associated with the formation of the $M^+{-}C_6F_6$ adduct ion. The lifetime of the intermediate $(M^+{-}C_6F_6)^*$ complex, and therefore the rate coefficient for association, is known to depend on this bond energy[18] and exclusively so for a family of addition reactions for which the degrees of freedom available for energy redisposition are the same, as is the case here. The efficiencies (derived from the apparent second-order rate coefficients) for addition of C_6F_6 to M^+ are generally quite high, >0.5. Cr^+ ($3d^5$), Mn^+ ($4s^13d^5$), Zn^+ ($4s^13d^{10}$), Mo^+ ($4d^5$), Ag^+ ($4d^{10}$), Cd^+ ($5s^1$-$4d^{10}$), and Re^+($6s^25d^4$) have efficiencies <0.31, and this suggests that these latter ions are bonded more weakly to C_6F_6. The special stability of half-filled and fully filled d valence shells toward covalent binding has already been noted, and this may account for these observations if covalent bonding predominates. But Cu^+ ($3d^{10}$) and Au^+ ($5d^{10}$) would then become exceptions in view of their high efficiencies for C_6F_6 addition.

Little is known about the nature and strengths of interactions between transition-metal ions and C_6F_6. Many modes of bonding (η^1, η^2, etc.) can be envisaged. Neutral complexes of transition metals and hexafluorobenzene that have been produced in the gas phase and condensed phase contain hexafluorobenzene coordinated η^6, η^4, η^3, or η^2 to the metal.[19−25] Also, C_6F_6 has been shown to be particularly effective as a ligand for η^4 and η^2 coordination at electron-rich metal centers in the solution phase.[23] The electrostatic potential of hexafluorobenzene has a positive value above the ring due to the electron-withdrawing capability of the fluorine atoms, leading to poor π binding sites for cations. Calculations have shown that in-plane fluorine-bridging binding sites are actually favored over π facial binding for the system $Cr^+ + C_6F_6$.[19] The binding energy of Cr^+ to the π face of hexafluorobenzene was calculated to be only 10.1 kcal mol^{-1} while the binding energy of Cr^+ to the fluorine-bridging binding sites is 20.4 kcal mol^{-1}.[19] The fluorine-bridging bonding is stabilized by in-plane σ(d−p)- and out-of-plane π(d−p)-orbital overlap.[26] A value of 34 ± 3 kcal mol^{-1} was found for $D(\mathrm{Au^+{-}C_6F_6})$.[22] B3LYP calculations have indicated that Au$^+$ is η^3 coordinated to the hexafluorobenzene plane in the most stable configuration of the gold cation−C_6F_6 adduct; an isomer with η^1-end-on coordination of Au$^+$ to a fluorine atom is only 4.6 kcal mol^{-1} less stable.[22]

Equilibrium was seen to be achieved in our experiments for the addition of C_6F_6 to Mn$^+$, Ag$^+$, and Cd$^+$ with corresponding values for ΔG°_{298} of −9.0, −10.6, and −8.0 kcal mol^{-1}, respectively.

Single Fluorine Atom Abstraction. Single fluorine atom transfer, reaction 7, contributed to 13 of the 29 reactions that were

$$\mathrm{M^+ + C_6F_6 \rightarrow MF^+ + C_6F_5} \qquad (7)$$

investigated with both early and late transition metal cations; it was usually a minor channel, ≤15%, but accounted for 30 and 50% of the reactive collisions of La$^+$ and Cd$^+$ with C_6F_6, respectively (see Table 1). Reaction 7 was observed with M$^+$ = Sc$^+$ (0.12), Y$^+$ (0.05), La$^+$ (0.30), Ta$^+$ (0.003), Cr$^+$ (0.05), Mn$^+$ (0.10), Fe$^+$ (0.05), Ni$^+$ (0.15), Pd$^+$ (0.10), Cu$^+$ (0.05), Ag$^+$ (0.10), Zn$^+$ (0.1), and Cd$^+$ (0.5) where the BR is given in parentheses. The occurrence of reaction 7 implies that the bond formed between the metal cation and fluorine is stronger than the C_6F_5−F bond being dissociated unless, of course, some internal excitation energy resides in the metal ion. A value of 116 ± 6 kcal mol^{-1} can be deduced for $D(\mathrm{C_6F_5{-}F})$ from a value for $\Delta H_f{}^0(\mathrm{C_6F_5}) = -128.6 \pm 4$ kcal mol^{-1} derived from the values given for $D(\mathrm{C_6F_5{-}H})$ and $\Delta H_f{}^0(\mathrm{C_6F_5H})$ in ref 27 (in the $C_6F_5^-$ anion section). For most of the metal cations, the thermochemistry of the single fluorine atom transfer reactions could not be calculated since M$^+$−F bond energies are rather poorly known. The only ones known, but not all that well, appear to be $D(\mathrm{Cr^+{-}F}) = 73$ kcal mol^{-1}, $D(\mathrm{Fe^+{-}F}) = 103 \pm 5$ kcal mol^{-1}, and $D(\mathrm{Ni^+{-}F}) \geq 109$ kcal mol^{-1}.[28] These values make reaction 7 endothermic for Cr$^+$ by about 43 ± 6 kcal mol^{-1} and for Fe$^+$ by 13 ± 11 kcal mol^{-1} for which we observe BRs for the F-atom transfer of 0.05. Consequently we may be observing small effects from residual excited states of the atomic ions produced in the ICP, at least for Cr$^+$ and Fe$^+$ since F-atom transfer with Ni$^+$ may still be exothermic or nearly thermoneutral. An analysis of the internal-energy population distribution at 5500 K for Cr$^+$ [13a,b] indicates that the states a^{4}D, a^{4}G, a^{4}P, and b^{4}D that account in total for 4.5% of the population have energies higher than 55.8 kcal mol^{-1} (more than the 43 ± 6 kcal mol^{-1} required for single F atom transfer). Similarly, the states a^{4}D and b^{4}P of Fe$^+$ account for 7.5% of the population at 5500 K and possess more than 22.1 kcal mol^{-1}, again more than the required 13 ± 11 kcal mol^{-1}. Finally, the a^{4}F state of Ni$^+$ alone accounts for 16.0% of the population and has more than 23.9 kcal mol^{-1} of energy compared with the (at most) 7 ± 6 kcal mol^{-1} required for single fluorine transfer. Therefore we cannot rule out the possibility that incomplete relaxation of excited states is responsible for the observed fluorine-transfer process with these metal cations. Indeed, in the case of Fe$^+$, previous FT-ICR measurements did not indicate fluorine-atom abstraction from C_6F_6.[6] The extent to which excited states contribute in the case of M$^+$ = Sc$^+$ (0.12), Y$^+$ (0.05), La$^+$ (0.3), Ta$^+$ (0.003), Mn$^+$ (0.10), Pd$^+$ (0.10), Cu$^+$ (0.05), Ag$^+$ (0.10), Zn$^+$ (0.10), and Cd$^+$ (0.50) is open to question since it is not known whether F-atom transfer is endothermic for these ions. We note, however, that the fractions of excited states present in the *initial population* at 5500 K for M$^+$ = Sc$^+$ (0.35), Y$^+$ (0.76), La$^+$ (0.59), Ta$^+$ (0.44), Mn$^+$ (0.16), Pd$^+$ (<0.4), Cu$^+$ (0.09), Ag$^+$ (0), Zn$^+$ (0), and Cd$^+$ (0) are those indicated in parentheses. So we can rule out completely the role of excited states only in the reactions of Ag$^+$, Zn$^+$, and Cd$^+$. Therefore our results indicate that $D(\mathrm{M^+{-}F}) > D(\mathrm{C_6F_5{-}F}) = 116 \pm 6$ kcal mol^{-1} for at least these three metals.

Multiple Fluorine Atom Abstraction. Group 3: Sc$^+$ (4s^{1}3d^1), Y$^+$ (5s^2), and La$^+$ (5d^2). Group 3 metal cations Sc$^+$ (4s^{1}3d^1), Y$^+$ (5s^2), and La$^+$ (5d^2), all of which have two valence electrons, react predominantly (BR = 0.57 (Sc$^+$), 0.95 (Y$^+$), and 0.70 (La$^+$)) by concerted abstraction of two fluorine atoms according to reaction 8. All three ions show a competing, but minor, F-atom transfer channel

$$\mathrm{M^+ + C_6F_6 \rightarrow MF_2{}^+ + (C_6F_4)} \qquad (8)$$

Experimental results for Sc$^+$ reacting with C_6F_6 are presented in Figure 1. FT-ICR measurements have provided similar results for gas-phase reactions of several lanthanide cations (Ce$^+$, Pr$^+$, Sm$^+$, Ho$^+$, and Tm$^+$) toward C_6F_6.[4,5] Single-defluorination was the competing channel except with Ho$^+$, which reacted exclusively to form HoF$_2{}^+$.

Neutral tetrafluorobenzyne C_6F_4 may be generated in our experiments concomitant with the formation of the ionized metal difluorides. Results from solution chemistry suggest that tetrafluorobenzyne is an intermediate in the activation of hexafluorobenzene by electron-deficient lanthanide complexes.[29] Alternatively, C_6F_4 may ring open and also fragment perhaps to give $C_2F_2 + C_4F_2$ or $C_6F_2 + F_2$.

The lack of thermochemical information for the species C_6F_4 prevents the determination of the exothermicities for reactions of type 8. The formation of MF$_2{}^+$ and C_6F_4 rather than $C_6F_4{}^+$ and MF$_2$ suggests that the ionization energy of C_6F_4 is higher than the ionization energies of ScF$_2$, YF$_2$, and LaF$_2$ (7, 7 ± 0.3, and 6.8 ± 0.3 eV, respectively).[17] There is less certainty associated with the relative value of IE(C_6F_4) and IE(ScF$_2$) because $C_6F_3{}^+$ formation, possibly due to the dissociation of $C_6F_4{}^+$, is associated with the reaction of Sc$^+$.

Two other product ions were identified for the reaction of Sc$^+$ with C_6F_6; formation of $C_6F_3{}^+$ accounts for 26% of the reactive collisions (reaction 9a) while generation of ScF$_3{}^+$ only for 5% (reaction 9b). Both product ions appear to be resulting from a triple defluorination of C_6F_6 by Sc. Transfer of two fluorine atoms to pair up the two valence electrons and one F$^-$ to neutralize the charge will produce ScF$_3$, and electron transfer from ScF$_3$ to $C_6F_3{}^+$ can occur subsequently as the products separate to produce ScF$_3{}^+$ and C_6F_3. If the observed BRs follow the reaction exothermicities, the larger BR for $C_6F_3{}^+$ indicates that process 9a has a higher exothermicity than process 9b and that IE(C_6F_3) ≤ IE(ScF$_3$)

$$\mathrm{Sc^+ + C_6F_6 \rightarrow C_6F_3{}^+ + ScF_3} \qquad (9a)$$

$$\mathrm{\rightarrow ScF_3{}^+ + C_6F_3} \qquad (9b)$$

We note here that the ground-state populations at 5500 K are 64.7, 24.2, and 40.6% for Sc$^+$(^{3}D), Y$^+$(^{1}S), and La$^+$(^{3}F), respectively.[13a,b] Taking into account the first excited states of these ions we can say that *at least* 83.1% of the Sc$^+$ ions will have energies below 0.6 eV, *at least* 78.8% of the Y$^+$ ions will have energies below 0.18 eV, and *at least* 67.2% of the La$^+$ ions will have energies below 0.40 eV. These are upper limits because they do not take into account any ion cooling between the ICP and the reaction region. Given the observed BRs for reaction 8 of 0.57 (Sc^+), 0.95 (Y^+), and 0.70 (La^+) and the maximum contributions of excited states (35.3% (Sc^+), 75.8% (Y^+), and 59.4% (La^+)), we can conclude that the concerted abstraction of two fluorine atoms from C_6H_6 is exothermic for ground-state $Sc^+(^3D)$, $Y^+(^1S)$, and $La^+(^3F)$.

Group 4: Ti^+ ($4s^13d^2$), Zr^+ ($5s^14d^2$), and Hf^+ ($6s^25d^1$). The major reaction pathway for metal cations from group 4 with C_6F_6 resulted in the formation of $C_6F_2^+$ (BR = 0.62 (Ti^+), 0.75 (Zr^+), and 0.87 (Hf^+)), most probably accompanied by generation of neutral MF_4, according to reaction 10. All three ions, each of which has three valence electrons, exhibit competing, but minor, two and three fluorine abstraction reaction channels. Experimental results for the reaction of Ti^+ with C_6F_6 are presented in Figure 3

$$M^+ + C_6F_6 \rightarrow C_6F_2^+ + MF_4 \tag{10}$$

Formation of MF_4 in reaction 10, very much thermodynamically favored over formation of the neutral combinations $MF_3 + F$, $MF_2 + F_2$, $MF + F_2 + F$, or $M + 2F_2$, is most interesting since it involves *the breaking and making of four chemical bonds in a single collision*. Presumably this reaction involves the pairing of the three valence electrons of M^+ with the electrons of three fluorine atoms and the transfer of a fluoride ion to neutralize the charge on M^+.

Some triple fluorine atom abstraction, which pairs up the three valence electrons of the group 4 cations along with formation of $C_6F_3^+$ by electron transfer upon separation of products according to reaction 11 was seen to occur for all three group

$$M^+ + C_6F_6 \rightarrow MF_3^+ + C_6F_3 \tag{11a}$$

$$\rightarrow MF_3 + C_6F_3^+ \tag{11b}$$

4 cations, albeit in different proportions. The higher BR observed for $C_6F_3^+$ formation than for TiF_3^+ formation suggests that $IE(C_6F_3) \leq IE(TiF_3) = 10.5 \pm 0.5$ eV.[17] The reaction of Zr^+ with C_6F_6 produced only ZrF_3^+, suggesting that $IE(C_6F_3) > IE(ZrF_3) = 7.5 \pm 0.5$ eV. Taken together, these two results suggest that $7.5 \pm 0.5 < IE(C_6F_3) < 10.5 \pm 0.5$ eV. Hf^+ did not show significant formation of either HfF_3^+ (3%) or $C_6F_3^+$(1%) and also exhibited the formation of small amounts of $C_6F_4^+$ (1%), $C_2F_3^+$ (1%), and $C_2F_4^+$ (4%), perhaps due to a higher than thermal internal energy content (see below).

We note that the ground-state populations at 5500 K are 44.0, 44.0, and 54.0% for Ti^+ (^4F), $Zr^+(^4F)$, and $Hf^+(^2D)$, respectively.[13a,b] Taking into account the first excited states of these ions, we can say that *at least* 79.1% of the Ti^+ ions will have energies below 0.15 eV, *at least* 55.6% of the Zr^+ ions will have energies below 0.47 eV, and *at least* 90.0% of the Hf^+ ions will have energies below 1.04 eV when these ions enter the reaction region. Given the observed BRs for reaction 10 of 0.62 (Ti^+), 0.75 (Zr^+), and 0.87 (Hf^+) and the maximum contributions of excited states (66.0% (Ti^+), 66.0% (Zr^+), and 46.0% (Hf^+)), we can conclude that reaction 10 is exothermic at least for ground-state $Hf^+(^2D)$ and for ground-state $Zr^+(^4F)$ as well.

Group 5: V^+ ($3d^4$), Nb^+ ($4d^4$), and Ta^+ ($6s^15d^3$). V^+ reacts with C_6F_6 mainly by simple addition (55%) and by two fluorine atom transfer to produce VF_2^+ (30%). However Nb^+ and Ta^+ reacted mainly by four fluorine atom abstraction to produce MF_4^+ (96.5 and 60%, respectively) according to reaction 12a

$$M^+ + C_6F_6 \rightarrow MF_4^+ + C_6F_2 \tag{12a}$$

$$\rightarrow MF_4 + C_6F_2^+ \tag{12b}$$

In the case of Ta^+, channel 12a was observed along with channel 12b. Three fluorine atom abstraction also was observed with all three group 5 ions and resulted mainly in $C_6F_3^+$ rather than MF_3^+ formation, suggesting that $IE(MF_3) \geq IE(C_6F_3)$ for M = V, Nb, and Ta. Ta^+ also exhibits some two fluorine atom transfer (0.3%), one fluorine atom transfer (0.3%), and some C−C bond insertion to produce $C_3F_3^+$ (17.5%) and $C_2F_3^+$ (0.5%). Raw data for the reaction of V^+ with C_6F_6 are shown in Figure 3.

We have reported and discussed previously the results for the remarkable reaction 12a observed between Nb^+ and C_6F_6.[11] This reaction involves the breaking of *four* C−F bonds and the making of *four* Nb−F bonds in one collision. This four fluorine atom transfer was proposed to proceed via an “unzipping” mechanism involving sequential intramolecular fluorine-atom transfer and initiated by a side-on approach of Nb^+ bridging two F atoms in the plane of the C_6F_6 ring. Experimental investigations of the reactions of Nb^+ with three isomers of tetrafluorobenzene and DFT computations at the B3LYP/DZVP level of theory appeared to discredit a possible mechanism via a face-on approach leading to concerted abstraction of four fluorine atoms.[11] Our calculations indicated that the overall reaction of Nb^+ (quintet ground state) and C_6F_6 (singlet ground state) to form difluorohexatriyne, C_6F_2, and NbF_4^+ (both singlets) is exothermic by 37.3 kcal mol^{-1} at 298 K.[11] The four fluorine atom transfer reported here for Ta^+ is likely to proceed in a similar fashion. Sequential intramolecular fluorine atom abstraction followed by dissociation of the collision complex at different stages can generate a variety of MF_x^+ product ions or MF_x neutral species, as observed in our experiments.

We note again the ground-state populations at 5500 K, in this case of 59.6% for V^+ (^5D), of 50.8% for Nb^+ (^5D), and of 56.4% for Ta^+ (^5F).[13a,b] Taking into account the first excited states of these ions, we can say that *at least* 88.9% of the V^+ ions will have energies below 0.39 eV, *at least* 76.6% of the Nb^+ ions will have energies below 0.51 eV, and *at least* 73.0% of the Ta^+ ions will have energies below 0.70 eV when these ions enter the reaction region. Given the observed BRs for reaction 12a of 0.965 (Nb^+) and 0.60 (Ta^+) and the maximum contributions of excited states (49.2% (Nb^+) and 43.6% (Ta^+)), we can conclude from our experimental observations that reaction 12a is exothermic for ground-state Nb^+ (^5D) and Ta^+ (^5F).

Group 6: Cr^+ ($3d^5$), Mo^+ ($4d^5$), and W^+ ($6s^15d^4$). Adduct formation becomes the predominant reaction channel with Cr^+ (95%) and Mo^+ (100%). Four fluorine atom abstraction also was observed, but only for the reaction of W^+ cation with C_6F_6, and resulted mainly in $C_6F_2^+$ formation (60%) via channel 12b as well as WF_4^+ formation (20%) via channel 12a.

Reactions Resulting in Concerted Activation of C−C and C−F Bonds. Reactions of the type 3 and 4 which lead to C−C and some C−F cleavage were observed only for the early third-row transition-metal cations Hf^+, Ta^+, and W^+ (see Table 1) but only in relatively small proportions, 5 and 3% for $Hf^+(5d^16s^2)$ and $W^+(5d^46s^1)$, respectively; only the reaction of $Ta^+(5d^36s^1)$ with C_6F_6 leading to $C_3F_3^+$ had a relatively large BR of 17.5%. Ring cleavage can be initiated by the insertion of the metal cations into the C−C bond.

While an argument that excited states of the metal cations are responsible for the observed ring cleavage can be invoked for our experimental conditions, it is surprising that other metal cations that also have potentially unquenched excited states at 5500 K did not present the ring cleavage pathway. It seems that the capability of third-row transition-metal cations to cleave aromatic rings is an intrinsic property of such ions determined mostly by their size and less by their electronic configurations.

The ions generated in reactions of type 3 are $C_2F_3^+$ (trifluorovinyl cation) and $C_2F_4^+$ (tetrafluoroethene cation). Neutrals of the form (MC_4F_3) and (MC_4F_2) or combinations such as $MC_2 + C_2F_3$ or $MC_2 + C_2F_2$ complement the formation of $C_2F_3^+$ and $C_2F_4^+$.

High-Order Reactions

Secondary and higher-order reactions were observed for many of the transition-metal ions investigated and were basically of three types: addition of C_6F_6, single fluorine transfer, and electron transfer.

Addition of hexafluorobenzene was observed to occur with C_6F_6 adducts formed in the primary step. Up to two molecules of C_6F_6 were observed to attach sequentially to all late transition-metal cations except Mn^+ and the very late transition metal cations Ag^+, Zn^+, and Cd^+, which added only one molecule of C_6F_6. Addition of C_6F_6 was also observed to occur with all other product ions formed in primary reactions. Two molecules of C_6F_6 added to ScF^+, YF^+, ScF_2^+, LaF_2^+, TiF_2^+, VF_2^+, and HfF_3^+ while only one molecule of C_6F_6 added to all other MF^+, MF_2^+, and MF_3^+ ions produced in primary reactions as well as to all MF_4^+, $C_6F_4^+$, $C_6F_3^+$, $C_6F_2^+$, and $C_2F_n^+$ generated in primary reactions.

As already indicated, C_6F_6 presents a multitude of binding possibilities with transition-metal cations ranging from symmetrical η^6 above the ring to a single covalent bond. There is essentially nothing known about the bonding of either one or two molecules of C_6F_6 in the adduct ions that we have observed here, probably for the first time. The highest coordination number that appears to be achieved in these complexes is five, with Hf^+ coordinated to three F atoms and two C_6F_6 molecules. Such a complex is isoelectronic with $VF_2(C_6F_6)_2^+$, also formed from sequential ligation of hexafluorobenzene to VF_2^+ with the asssumption that C_6F_6 binds in the same manner to both metal cations. If these complexes achieve coordinative saturation, it can be deduced that the coordination of hexafluorobenzene with metal cations involves six electrons, presumably having the metal cation situated above the π system of C_6F_6. However, there is no clear indication that further addition of C_6F_6 to $HfF_3(C_6F_6)_2^+$ and $VF_2(C_6F_6)_2^+$ is not discriminated against experimentally due to a very low binding energy.

Single fluorine transfer was observed to occur as a secondary or higher-order reaction. Five cases were identified with certainty by combining information from the flow-dependent reaction profiles with flow-dependent BR plots. The primary product ScF_2^+ generates ScF_3^+ (partly also a primary product), which in turn generates ScF_4^+. Also, LaF^+ produces LaF_2^+ (partly also a primary product) and then generates LaF_3^+. TaF_3^+ generates TaF_4^+ (partly also a primary product). NiF^+ generates NiF_2^+. CuF^+ gives CuF_2^+ that produces CuF_3^+.

Electron transfer was observed to occur as a secondary reaction; $C_6F_6^+$ was formed as a secondary product from the reaction of $C_6F_3^+$ and $C_6F_2^+$ with C_6F_6. If the product $C_6F_3^+$ and $C_6F_2^+$ ions undergo a sufficient number of collisions with He atoms to become thermalized prior to colliding with C_6F_6, this result implies that the species C_6F_3 and C_6F_2 possess ionization energies higher than $IE(C_6F_6) = 9.90 \pm 0.04$ eV. Furthermore, the constraints for $7.5 \pm 0.5 \text{ eV} < IE(C_6F_3) < 10.5 \pm 0.5$ eV can be further increased to $9.90 \pm 0.04 < IE(C_6F_3) < 10.5 \pm 0.5$ eV.

Comparison of the Metal Ion Chemistry with C_6H_6 and C_6F_6

The chemistry of transition-metal cations toward benzene has been previously investigated in our laboratory.[33] Fast addition of benzene (close to the collision rate) was the exclusive primary reaction pathway for most transition-metal cations; only Ta^+ initiated the cleavage of the benzene ring to generate primarily $TaC_4H_4^+$ and neutral C_2H_2. The versatile chemistry reported here for reactions of hexafluorobenzene with transition-metal cations reflects the relatively high affinity of metal cations toward fluorine atoms. Even though the C−F bond in C_6F_6 is stronger than the C−H bond in C_6H_6,[2] activation of the C−F was observed as a predominant reaction pathway in reactions of several metal cations with C_6F_6, while C−H bond activation was observed only as a minor channel in the reaction of Ta^+ with C_6H_6.

The bonding of transition-metal cations with benzene has been extensively studied, both experimentally and theoretically.[30−32] The bonding is described as being predominantly electrostatic, with important contributions from electron promotion, hybridization, and orientation of the singly or doubly occupied d orbitals on the metal ion and metal d−π^* donation.[30] DFT calculations[32] have shown that most benzene adducts of first-row transition-metal cations have C_{6v} symmetry (η^6 coordination) with the metal cation situated symmetrically above the benzene ring. Exceptions are the V^+, Ni^+, and Fe^+ complexes which have only C_{2v} symmetry due to modest Jahn−Teller-induced boat-shaped distortions of the benzene ligand.[32] $AgC_6H_6^+$ has only C_s symmetry because Ag^+ is not situated symmetrically above the benzene ring but moves closer to one pair of carbon atoms.[30] Most transition-metal cations form sandwich bisadducts with benzene in which the second molecule of benzene is more loosely bound than the first one and possibly involved only in a η^4 coordination with the metal cation.[31]

The nature and strength of the interaction between transition-metal ions and hexafluorobenzene is not well known but has been compared in the literature with the coordination of metal cations toward benzene.[19,21,22,26] Electrostatic arguments point to possible differences in the binding mode of metal cations to hexafluorobenzene and benzene. While the electrostatic potential of benzene has a negative value above the ring, thus providing a good π binding site for cations, the electrostatic potential of hexafluorobenzene presents a positive value above the ring due to the electron-withdrawing capability of the fluorine atoms, thus leading to poor π binding site for cations. Calculations have shown that in-plane fluorine bridging binding sites are actually favored over π-facial binding for the system $Cr^+ + C_6F_6$.[19] The binding energy of Cr^+ to the π face of hexafluorobenzene was calculated to be only 10.1 kcal mol^{-1} (with zero-point energy corrections), while the binding energy of Cr^+ to the fluorine-bridging binding sites is 20.4 kcal mol^{-1}.[19] The fluorine-bridging bonding is stabilized by in-plane σ(d−p) and out-of-plane π(d−p) orbital overlap.[26] In contrast, the coordination of Cr^+ to the π face of benzene was found to lead to a much stronger bond with a bond-dissociation energy of 39.5 kcal mol^{-1}.[19] The effect of the electron-withdrawing properties of the fluorine atoms in C_6F_6 was assessed from bond-dissociation energy determinations for the system $AuC_6F_6^+$.[21,22] A value of 34 ± 3 kcal mol^{-1} was found for $D_0^{298}(Au^+{-}C_6F_6)$ in comparison with $D_0^{298}(Au^+{-}C_6H_6) = 69$ kcal mol^{-1},[22] indicating that the substitution of hydrogen atoms with fluorine atoms reduces the bond energy of gold cations to benzene in half. B3LYP calculations indicated that the most stable configuration of the gold cation$-C_6F_6$ adduct has Au^+ η^3 coordinated to hexafluorobenzene above the ring plane.[22]

Conclusions

The results of our systematic study on the reactivity of transition-metal cations toward hexafluorobenzene reveal trends across the periodic table with regard to both the type of chemistry and the reaction efficiency.

The reactions of early transition metal cations (groups 3−5 and W^+) with C_6F_6 occur at or close to the collision limit and are dominated by multiple fluorine transfer resulting in formation of ionized species MF_n^+ and/or $C_6F_{6-n}^+$ with $n = 1-4$. A competition of several primary channels, most of which involve multiple fluorine transfer, is observed for reactions of early transition metal cations. The maximum number of fluorine atoms being transferred in one reaction step equals the number of electrons present in the valence shell of the transition metal.

The multiple fluorine abstraction reactions observed are proposed to occur via a mechanism involving sequential intramolecular fluorine atom abstraction initiated by the formation of a long-lived intermediate.

The chemistry of late transition metal cations with hexafluorobenzene is dominated by simple addition of up to two molecules of C_6F_6. Single fluorine transfer and electron transfer compete with addition in some instances. The reaction efficiencies for addition show trends across the periodic table which reflect differences in binding energies due to differences in the electronic structure of the transition-metal ion.

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