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Notes

Multiple C−F Bond Activation: Remarkable 4 to 4 Bond-Breaking/Bond-Making Reactions of Nb^+ with Hexafluoro- and Tetrafluorobenzene

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Summary: Mass spectrometric reaction rate measurements are reported that show the remarkable occurrence of the breaking of four C−F bonds and the formation of four new Nb^+−F bonds in gas-phase collisions of Nb^+ with hexafluoro- and tetrafluorobenzene. A mechanism involving sequential intramolecular fluorine pick-up is proposed.

Introduction

Chemistry is about the making and breaking of bonds, commonly one at a time. Multiple bond-breaking/bond-making reactions are less common. We report here the remarkable experimental observation of gas-phase reactions of thermalized Nb^+ with hexafluorobenzene and tetrafluorobenzene leading to multiple C−F bond activation and a transfer of *four* fluorine atoms as illustrated in reaction 1. Our kinetic measurements have

$$Nb^+ + C_6F_6 \rightarrow NbF_4^+ + (C_6F_2) \qquad (1)$$

demonstrated that these processes are one-collision events and involve the breaking of four C−F bonds and the formation of four new Nb^+−F bonds. C−F bond activation by bare-metal monocations in the gas phase,[1−6] and by metal complexes in solution,[7] is being investigated with increasing vigor given the possible role of fluorocarbons in greenhouse warming and the important applications of fluorocarbons in industry.

Ca^+ and selected lanthanide cations (Ce^+, Pr^+, Sm^+, Ho^+, and Tm^+) have been shown to abstract F from hexafluorobenzene in the gas phase.[2−4] Ce^+, Pr^+, Sm^+, and Tm^+ promote both single and double defluorination from hexafluorobenzene, while Ho^+ reacts exclusively by double defluorination.[3]

A process analogous to reaction 1 involving multiple S−F bond activation has been reported previously by Freiser and co-workers,[8] who observed formation of NbF_4^+ when Nb^+ was exposed to SF_6 in an ICR mass spectrometer. Also, the transition metal cations Ti^+, Cr^+, Fe^+, Mo^+, and W^+ have been observed to undergo multiple fluorine atom abstraction from a fluorinated self-assembled monolayer surface in low-energy (<100 eV) ion/surface collision experiments.[5,6]

Experimental Section

The experiments were performed with our newly configured inductively-coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer[9,10] as part of a survey of periodic chemical reactivities of atomic ions with hexafluorobenzene. The atomic ions were generated in an argon plasma at 5500 K fed with an aerosol containing the metal. They 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 ± 0.01 Torr and 295 ± 2 K. After experiencing about 10^5 collisions with He atoms, the ions were allowed to react with added hexafluorobenzene or tetrafluorobenzene. The reacting mixture was sampled still further downstream by a second quadrupole mass spectrometer, and reactant and product ions were measured as a function of added reactant. The resulting ion profiles provide information about product ion distribution, reaction rate coefficients, and reaction molecularity. The atomic ions emerging from the atmospheric pressure plasma have a Maxwell−Boltzmann internal energy distribution characteristic of the plasma temperature of 5500 K, which can be calculated from known energy levels.[11] For Nb^+ the initial distribution is ^5D (51%) at 0−0.15 eV, ^5F (26%) at 0.3−0.5 eV, ^3P (7%) at 0.7−0.9 eV, ^3F (4.4%) at 0.9−1.0 eV, ^3H (4.4%) at 1.2−1.3 eV, and a further

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Table 1. Measured Reaction Rate Coefficients (k_{obs}), Collision Rate Coefficients (k_c), Reaction Efficiencies (k_{obs}/k_c), Product Ions, and Product Ion Distributions for Reactions of Nb^+ with C_6F_6, 1,2,3,4-$C_6H_2F_4$, 1,2,3,5-$C_6H_2F_4$, and 1,2,4,5-$C_6H_2F_4$ in He at 0.35 ± 0.1 Torr and 295 ± 2 K

neutral reagent	k_{obs} (cm^3 molecule^{-1} s^{-1})[a]	k_c (cm^3 molecule^{-1} s^{-1})[b]	k_{obs}/k_c[a]	product ion	product ion distribution[c]
C_6F_6	8.6×10^{-10}	9.21×10^{-10}	0.93	NbF_4^+	96.5%
				NbF_3^+	1.5%
				$C_6F_3^+$	1.5%
				$NbC_6F_6^+$	0.5%
1,2,3,4-$C_6H_2F_4$	1.8×10^{-9}	2.0×10^{-9}	0.90	NbF_4^+	80.0%
				$C_3F_2^+$	15.0%
				$NbC_4F_4^+$	2.5%
				$NbC_4HF_3^+$	2.5%
1,2,3,5-$C_6H_2F_4$	8.1×10^{-10}	9.6×10^{-10}	0.84	NbF_4^+	85.0%
				$C_3F_2^+$	10.0%
				$NbC_4HF_3^+$	5.0%
1,2,4,5-$C_6H_2F_4$	1.4×10^{-9}	1.4×10^{-9}	1.0	NbF_4^+	80.0%
				$C_3F_2^+$	15.0%
				$NbC_2F_4^+$	5.0%

[a] Uncertainties in the measured reaction rate coefficients are estimated to be ±30%. [b] Calculated using the algorithm of the combined variational transition-state theory developed by Su and Chesnavich.[12] [c] Branching ratios are rounded off to the nearest 0.5% and have an uncertainty estimated to be ±10%.

7.2% with energies up to 2.44 eV, but this population is downgraded by collisions with argon atoms during sampling, by collisions with He atoms in the flow tube, and by radiative decay before entry into the reaction region. The final population is not known.

Rate coefficients for the primary reactions were determined in the usual manner from the rate of decay of the reactant ion intensity with added neutral reagent (with an uncertainty estimated to be less than ±30%). Rate coefficients for secondary and higher-order reactions were obtained by fitting the experimental data to solutions of differential equations for successive reactions. Measured branching ratios (percentages) for primary reactions with more than one product were rounded off to the nearest 0.5%.

Neutral reagents were introduced into the reaction region as vapors diluted in helium to various levels. The reagents were obtained commercially and were of high purity (99.9% C_6F_6, 99+% 1,2,4,5-$C_6H_2F_4$, 99% 1,2,3,4-$C_6H_2F_4$, 95% 1,2,3,5-$C_6H_2F_4$). The neutral reagents were used without further purification, except for multiple freeze−pump−thaw cycles to remove noncondensable gases.

Results and Discussion

While scanning atomic ion reactivities across the periodic table, we noticed that Nb^+ reacts rapidly with C_6F_6, $k_{obs} = 8.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, at essentially the collision rate (see Table 1) to produce NbF_4^+ product ions in a single-collision event according to reaction 1. Supporting data are shown in Figure 1. Other, although minor (<5%), primary reaction channels also were observed, leading to a variety of other product ions, as illustrated in reactions 2a through 2c with the branching ratios shown in Table 1.

$$Nb^+ + C_6F_6 \rightarrow NbF_3^+ + (C_6F_3) \quad (2a)$$

$$\rightarrow C_6F_3^+ + NbF_3 \quad (2b)$$

$$\rightarrow NbC_6F_6^+ \quad (2c)$$

Formation of NbF_4^+ accounts for 96.5% of the reactive collisions between Nb^+ and C_6F_6. Channels 2a and 2b correspond to the transfer of three F atoms without and with electron transfer upon product separation, respectively. Channel 2c corresponds to addition, presumably via a termolecular reaction with He as the third body.

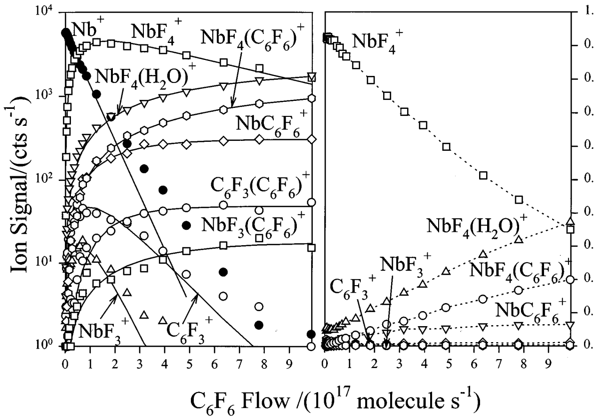

Figure 1. Left: Reactant and product ion intensities observed for the reaction of Nb^+ with C_6F_6 as a function of C_6F_6 flow. The solid lines represent a fit of the experimental data points with the solutions of the differential equations appropriate for the observed reactions. Right: Plot of fractional abundances of ionized products as a function of the C_6F_6 flow. The zero-flow intercepts of these plots provide the branching ratios for the primary reaction products listed in Table 1. $NbF_4(H_2O)^+$ is formed by the direct addition of H_2O to NbF_4^+ and the exchange with C_6F_6 in $NbF_4(C_6F_6)^+$; H_2O is present in trace amounts in the buffer gas.

As indicated in the Experimental Section, there is some uncertainty regarding the electronic state of the Nb^+ in the reaction region, but since at least 51% of the Nb^+ emerging from the ICP source are in the ground ^5D state, the bulk (if not all) of the formation of NbF_4^+ must be attributed to this state. The slight curvature in the semilogarithmic decay of Nb^+ in Figure 1 may be indicative of the presence of some exited states with different reactivities but may also arise from the occurrence of the reverse of reaction 2c. Higher-order chemistry was also observed; NbF_4^+, NbF_3^+, and $C_6F_3^+$ reacted further to add C_6F_6 and produce $NbF_4(C_6F_6)^+$, $NbF_3(C_6F_6)^+$, and $C_{12}F_9^+$, respectively.

To explore the influence of the *arrangement* of the four fluorine atoms around the aromatic ring on reactivity, separate experiments were performed to measure the reactivity of Nb^+ toward the isomers 1,2,3,4-tetrafluorobenzene, 1,2,3,5-tetrafluorobenzene, and 1,2,4,5-tetrafluorobenzene. The measured rate coefficients and branching ratios of observed primary reaction channels for all three isomers are included in Table 1. The four-fluorine atom abstraction channel (again) was observed to be the predominant primary channel *with all three isomers*. The branching ratio for this channel was similar for all three isomers (80−85%), indicating no preference for a particular arrangement of the fluorine atoms in tetrafluorobenzene. Other primary reactions, all leading to C−C activation and the dissociation of the aromatic ring, were observed to compete with 4F transfer to a small extent. Dissociation to produce $C_3F_2^+$ and $[NbC_3H_2F_2]$ was the major competing channel of this type (10−15%) observed with all three isomers of tetrafluorobenzene. Other observed channels led to the elimination of $[C_2H_2]$, $[C_2HF]$, and $[C_4H_2]$. Addition and electron transfer dominated the higher-order chemistry with the three isomers of tetrafluorobenzene. Electron transfer was observed only with NbF_4^+ and in competition with other reaction channels with branching ratios of 0.05, 0.10, and 0.30 for 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-$C_6H_2F_4$, respectively. These observations, together with the failure to observe electron transfer between NbF_4^+ and C_6F_6, imply a value for $IE(NbF_4) = 9.74 \pm 0.20$ eV based on $IE(C_6F_6) = 9.90 \pm 0.04$ eV and IE(1,2,3,4-$C_6H_2F_4$) $= 9.57 \pm 0.03$ eV.[13] We are not aware of a previous experimental or theoretical determination of this ionization energy.

The mechanism of the 4 to 4 bond-breaking/bond-making reaction 1 is most intriguing. The accompanying bond redisposition can be envisaged to involve anything from a concerted "pick-up" of four F atoms to the sequential intramolecular "unzipping" of four F atoms one or more at a time. Our B3LYP/DZVP calculations (see below) have shown that for all of the singlet, triplet, and quintet electronic configurations of the Nb^+ face-on adducts with C_6F_6 the binding occurs by interaction of Nb^+ with the carbon skeleton of C_6F_6 and not with fluorine atoms or C−F bonds. Actually, two or more fluorine atoms are being pushed away from Nb^+ during adduct formation. Therefore, a concerted removal of four fluorine atoms is not a favorable mechanistic pathway; the interaction of Nb^+ with four fluorine atoms of C_6F_6 would proceed through a channel requiring considerable activation energy. The predominant occurrence of NbF_4^+ formation with all three isomers of tetrafluorobenzene with essentially identical branching ratios (see Table 1) points also to a sequential intramolecular unzipping mechanism rather than to a concerted pick-up of four fluorine atoms. The concomitant removal of four fluorine atoms is likely to be connected with a certain arrangement of the fluorine atoms in tetrafluorobenzene and is unlikely to occur with equal ease from all three isomers of tetrafluorobenzene.

The mechanism of multiple fluorine atom abstraction observed by Freiser et al. in reactions of early transition metal cations, M^+, with SF_6 was proposed to occur via sequential intramolecular F transfer from S to M^+ within a long-lived intermediate $[M\cdots SF_6]^+$. The formation of such an intermediate is possible with early transition metal cations that have at least one empty d orbital available.[8] A similar mechanism is conceivable for the reactions of Nb^+ with C_6F_6. The metal cation can attack the hexafluorobenzene molecule by bridging two fluorine atoms in the plane of the ring by using its empty d and a p orbital, to generate a collision complex with a long lifetime. Whether such attack is initiated from the side of C_6F_6 to two adjacent fluorine atoms or from a face-on attack to the π face of C_6F_6 is not known. Metal cation insertion into C−F bonds or simply the weakening of C−F bonds upon coordination with Nb^+ precedes the cleavage of the C−F bonds. Subsequently, the Nb^+ cation with one or two fluorine atoms attached either "rolls around" the ring or "spins above" the ring to approach other F atoms. Sequential Nb^+ cation insertion into C−F bonds followed by C−Nb bond cleavage can ensue, and dissociation of the collision complex at different stages can generate a variety of NbF_x^+ product ions, as observed in our experiments.

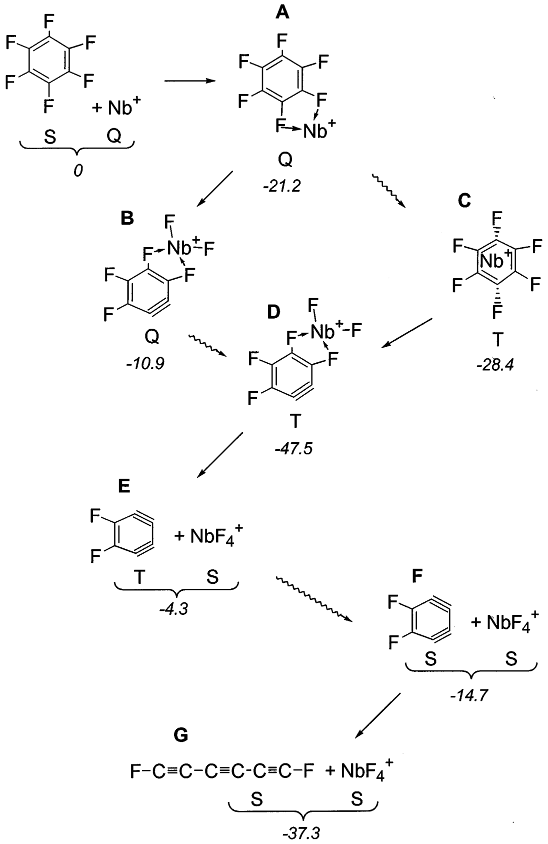

Figure 2. Possible mechanism for 4F transfer from C_6F_6 to Nb^+. Computed relative enthalpies of intermediates and products at 298 K with respect to the enthalpy of the reactants are indicated in kcal mol^{-1}. They were computed at the B3LYP/DZVP level of theory. The multiplicities of the computed structures are also indicated as S (singlet), T (triplet), and Q (quartet).

Figure 2 presents a possible mechanistic path for reaction 1 based on our computations. Computations performed at B3LYP/DZVP[14−20] using the Gaussian

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suite of programs[21] indicate that the enthalpy at 298 K for the reaction of Nb^+ (quintet ground state) and C_6F_6 (singlet ground state) to form difluorohexatriyne and NbF_4^+ (both singlets) is exothermic by 37.3 kcal mol^{-1}. The initial adduct in the quintet state, formed by in-plane complexation with two F atoms (structure **A**), may either rearrange to $C_6F_4 \cdot NbF_2^+$ (structure **B**) or undergo intersystem crossing to form the triplet state adduct (structure **C**). The latter is the lowest energy adduct of C_6F_6 with Nb^+, but its formation involves considerable rearrangement.

The next step is for ion **B** or **C** to rearrange to ion **D**, tetrafluorobenzyne complexed to NbF_2^+. Ion **D** has the lowest energy on the potential energy hypersurface, but when formed will be thermally very hot and rearranges to 1,2-difluorobenzdiyne **E** (in its triplet state) plus NbF_4^+ (in its singlet state). This combination of products is only 4.3 kcal mol^{-1} below that of the initial reactants. The high-energy difluorodibenzyne molecule then rearranges by intersystem crossing to form the singlet difluorobenzdiyne **F** followed by ring opening to form the difluorohexatriyne **G** in its singlet state. It is interesting to note in this regard that both ring isomer 3,6-difluoro-1,4-benzdiyne and the linear isomer 1,6-difluorohexatriyene very recently have been observed directly by wavelength selective photolysis of benzenetetracarboxylic dianhydride in low-temperature nitrogen matrixes.[22]

We have now explored the chemistry of C_6F_6 with about 30 other atomic ions, and only Ta^+ and W^+ (in addition to Nb^+) exhibited MF_4^+ formation according to reaction 1. The results of these latter studies will be reported separately.

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