Three-Membered Cyclic Fluoronium Ions in Gaseous Ion–Neutral Complexes

Viet Nguyen, Xueheng Cheng, and Thomas Hellman Morton*

Contribution from the Department of Chemistry, University of California, Riverside, California 92521-0403. Received September 30, 1991. Revised Manuscript Received February 25, 1992

Abstract: The fluoriranium ion (CH2CH2F+, 1a) is shown to exist as an intermediate within ion–neutral complexes derived from the molecular ions of β-fluorophenetole (8+). Ion–neutral complexes containing the isomeric ion CH2CHF+ (2a) also occur. The parent neutral 8 favors the gauche conformation, and theoretical calculations show that the radical cation 8+ and the conjugate acid ions should also favor their gauche conformers. NMR analysis of the neutral fluoroethylenes from deuterated analogues of 8+ show that fluorine bridging to form 1a and hydrate shift to form 2a take place competitively and not sequentially. Nearly the same ratios of CH2DF loss to CH2HDF loss are observed for the radical cations and from the MD+ conjugate acid ions. By contrast, free CH3C2H5D+ ions quenched by chloride abstraction from (CH3)2CCl have the structure 2a, in which sequential transpositions have occurred. The difference between free ions and ions within complexes is ascribed to the millionfold difference in lifetimes under the experimental conditions.

Cyclic halonium ions have a long history as intermediates in organic chemistry. Bridged structures are well-known for other halogens, but the case of X = fluorine has heretofore proven elusive. When X = chlorine or bromine, the energetics of isomerization via hydride shift to form α-haloethyl cations, drawn in organic chemistry. Bridged structures are well-known for other elusive. When

three heats of formation, but only 2b is observed by low-temperature matrix isolation.1 Ions 1c and 2c (X = Br) are also close in energy, but only 1c is observed under the same conditions. For X = F, ab initio2 and empirical estimates3,4 place 2a, which is a stable ion in the gas phase,3,4 70 kJ mol\(^{-1}\) (17 kcal mol\(^{-1}\)) lower than 1a, and the latter has never been observed directly.

We describe here a reaction that produces 1a and 2a competitively in the gas phase under conditions where the interconversion depicted in eq 1 does not take place. Previous efforts to produce 1a or its higher homologues5,6 show products in which fluorine transposes (consistent with the intermediacy of epifluoronium ions), but the species that have been detected are the products of subsequent rearrangement. For instance, the mass spectrometric evidence that a free fluoroethyl cation might pass through 1a hinges upon its expulsion of a methyl radical,6 which means that the ion observed to decompose must have been 2a. This raises the question as to whether cyclic fluoronium ions are stable structures or transition states.

The same question is raised by studies of fluorine transposition within positive ions in ion–neutral complexes. Electron impact on alkyl phenyl ethers generates complexes in which the alkyl moiety undergoes rearrangements as though it were a free cation that lives for a very short time. When the starting neutral is a 1-phenoxalkane, cleavage of the C-O bond would have generated a primary cation. Therefore, complexes are formed that contain a rearranged alkyl cation and a phenoxy radical. Typically, simple rearrangements occur (such as hydride or alkyl shifts). Deep-seated isomerizations (e.g. s-Bu → t-Bu, cyclohexyl → 1-methyleclopentyl, or CH3CH2CHF → (CH3)2CF) tend not to be observed, owing to the brief lifetimes (estimated on the order of 1 ns) of ion–neutral complexes.8

When mono-fluoroalkyl phenyl ethers are ionized, complexes are formed that contain fluoroalkylyl cations. The electron bombardment flow (EBFlow) reactor allows us to collect the neutral products that result from the unimolecular decomposition of the complexes at pressures on the order of 10\(^{-4}\) Torr and to analyze them using NMR spectroscopy.9 As eq 2 depicts, previous studies have shown neutral products (e.g. 5) that provide evidence for fluoride shift. Isotopic labeling of neutral starting materials 3 and 4 shows that the transposition (which occurs competitively with methyl or hydride shift) does not occur via elimination of HF (to form an allylic cation) followed by readdition.5,7 Furthermore, the distribution of \(^1\)C from labeled 3 informs us that the intermediate CH3CFD+ does experience reversible hydrogen shifts but does not have time to undergo a deep-seated rearrangement to its most stable isomer (even though free fluoro-propyl cations do so extensively on the 1-ms time scale).

The experiments summarized by eq 2 warrant the inference that fluorine is capable of transposing via three-membered cyclic fluoronium ions 6. The available data do not tell us whether such a structure is an intermediate or a transition state or whether it intervenes when alternative mechanisms are possible. For example, transposition in the intermediate derived from 3 might have occurred via a structure such as 7, which can be viewed as being

---

isoelectronic with a van der Waals complex of water with propylene. While this kind of structure (which would transpose hydrogen at the same time as fluorine) cannot be definitively ruled out for 3, such a structure is not possible for 4.

This paper presents a comparison of the behavior of free fluoroethyl cations in the gas phase with the behavior of those that are formed in ion-neutral complexes. Our study answers two questions about fluorine transposition in a fluoroethyl cation, the simplest system in which fluorine can bridge. The first is whether fluorine transposes with concomitant transposition of hydrogen (e.g. via structures such as 7). The answer to this question is negative. The second is whether the bridged ion corresponds to a discrete intermediate. Here we conclude that the answer is affirmative.

Experimental Section

The EBFlow technique has been described in detail elsewhere. In brief, gaseous substrates (in the pressure range 10^-4-10^-3 Torr) are subjected to bombardment by 70-eV electrons (currents on the order of 10^-5-10^-4 A) while flowing from a sample bulb into a liquid-nitrogen-cooled trap. The reaction vessel is housed in a solenoid electromagnet (flux density on the order of 0.2 T), which focuses the electron beam on an axis and helps keep ions from striking the walls. Electrically charged species exit the reaction vessel into a separate, differentially pumped chamber, where the products from their neutralization are removed and do not contaminate the neutral products recovered from the reaction vessel. Recovered neutral product mixtures were analyzed by 470-MHz 19F NMR spectroscopy on a General Electric GN500 instrument. The isomeruomers of fluoroethane were identified by their 19F-H spin-spin couplings.

Mass spectra were recorded on a VG ZAB 2F (B-E), on a VG 7070 (E-B), and on an HP 5989A quadrupole on-line with a HP 5990 gas chromatograph. Chemical ionization mass spectra were performed by introducing deuterium gas (Cambridge Isotope Laboratories) into the ZAB source. All initial calculations were performed using the SPARTAN software on a Silicon Graphics 4D/35 Personal Iris Computer. The proton-proton spin-spin splitting patterns were simulated using the LAOCOON program.

Materials

Unless otherwise specified, starting materials were used as received from commercial suppliers without further purification. Deuterated 2-bromo-1-fluoroethane was prepared by reaction of BrC-H,CD-OH (from reduction of methyl bromoacetate with LiAIH4) with (diethyldiamino)sulfur trifluoride (DAST) and consisted of a 92/8 mixture BrCH2CH2F and BrCD2CH2F.

2-Fluoroethyl Phenyl Ethers (8).

2-Fluoroethyl phenyl ethers (8) were isolated from the deuterated 2-bromo-1-fluoroethane by reaction with DAST in CH2Cl2. After distillation and screening for GPC, 2-Phenoxy-2,2-dideuterio-1-fluoroethane (8c) was prepared by reaction of 2-fluoroethyl phenyl ethers (8) with LiAIH4 reduction of phenoxyacetic acid) was converted to 2-phenoxy-2,2-dideuterio-1-fluoroethane (8c) with (diethyldiamino)sulfur trifluoride (DAST) and consisted of a 92/8 mixture BrCH2CH2F and BrCD2CH2F.

Results

One of the hallmarks of ion-neutral complexes formed from ionized alkyl phenyl ethers is the parallelism between alkene loss from radical cations (even-electron ions) and alkene loss from conjugate acid ions (even-electron cations). This was first reported in 1976 by Benoit and Harrison, who observed that expulsion of isotopically labeled propenes from various deuterated n-propyl phenyl ethers follows nearly the same pattern under conditions of electron impact (which forms radical cations) and chemical ionization (which forms the conjugate acid ions). This similarity is readily explained by a complex-mediated mechanism, since the rearrangements of cations within complexes should not depend upon the identity of the leaving group, and the distribution of deuterium in the products should depend only on its protein affinity.

The congruence of electron impact (EI) and chemical ionization (CI) results is hard to explain without invoking intermediate complexes. Results from the literature for n-propyl phenyl ethers (X = CH3) are summarized in eq 3, which shows complete unimolecular scrambling of all the alkyl hydrogens. (The results for D3+ chemical ionization have not been reported; the approximate ion ratios are interpolated from the reported data for chemical ionization using H3+, CH3+,[12] and CD3+ reagent gases.) It is worth noting that the same results for the radical cation decompositions have been observed on the shortest timescale (10-11 s) measurable by field ionization kinetics.[14] This implies


(10) SPARTAN: Wavefunction Inc.: Irvine, CA.


Fluorine Ions in Gaseous Ion–Neutral Complexes

that ion–neutral complexes can form very promptly after ionization.

The 2-fluoroethyl phenyl ethers \( X = F, 8 \) also exhibit a striking similarity in their electron impact (EI) and chemical ionization (CI) mass spectra. The undeuterated compound \( 8a \) gives a 70-eV electron impact mass spectrum in which PhOH\(^+\) \( [M-CH_3=CHF]^+ \) constitutes the base peak, approximately 30% of the total ionization. The principal fragment ions in the \( D_2^+ \) chemical ionization mass spectrum are \([MD-CH_3=CHF]^+ \) and \([MD-DF]^+ \) in a ratio of 100/80. \( D_2^+ \) ion intensity is sensitive to source pressure: reported fragment ion ratios correspond to spectra in which the intensity of that ion is less than or equal to one-fifth the intensity of the base peak.) While a small amount of exchange between \( D^+ \) and the alkyl chain (0.09 times the base peak intensity) has been reported in the CI mass spectrum of \( -\text{CHCH}_2\text{Fl} \), such exchange occurs to a much lesser extent (\( \leq 0.05 \) times the base peak intensity) in \( 8a \). This is in keeping with expectation, as phenol has a proton affinity 90 kJ mol\(^{-1}\) greater than that of the expelled fluoroethylene (while the difference between the proton affinities of phenol and propane is only 70 kJ mol\(^{-1}\)). Since the exchange between \( D^+ \) and the alkyl chain has been shown to occur via reversible proton transfer within ion–neutral complexes, \(^{13} \) it stands to reason that the contribution from the back-reaction will decrease as the exothermicity of proton transfer increases.

We observe the same proportions of PhOH\(^+\) and PhOD\(^+\) in the 70-eV electron impact mass spectrom of PhOC\(\text{H}_2\text{CD}_2\text{F} \) and PhOC\(\text{H}_2\text{CH}_2\text{F} \) (8e) (allowing for minor variations from instrument to instrument), as previously reported by Nibbering and co-workers. \(^{16} \) The ratios of \( C_2H_2DF \) loss to \( C_2H_2F \) loss that we observe in the \( D_2^+ \) CI spectra are compared with the published EI results in eq 3. The principal fragment ions from \( D_2^+ \) CI mass spectroscopy of \( 8b \) are \([MD-CH_3=CHF]^+ \), \([MD-CH_2=CHF]^+ \), and \([MD-DF]^+ \) in a ratio (corrected for 13C natural abundance) of \( m/z 96:97:123 = 82:52:100 \). The same ions are seen from \( 8c \) in a ratio of \( m/z 96:97:123 = 65:65:100 \) (corrected for 13C natural abundance).

We inquire as to whether the similarity of EI and CI spectra reflects an inherent similarity in the conformer distribution of the parent ions. Neutral \( 8 \) is expected to have two predominant conformers: a Planar one, in which the phenoxy and fluorine are anti, and a \( \perp \) pair, in which these functional groups are favor the anti conformation (SCF calculations with even small basis sets give an FCCF dihedral angle close to the value of 74°). The calculated dihedral angles are summarized in Figure 1. The anti conformer approaches \( C_2\) symmetry, even though \( J_{CH:F} = 8.3 \text{ Hz} \) and \( J_{H:F} = 9.1 \text{ Hz} \) and the dihedral angles (°) that we calculated for 2-fluoroethanol at 3-21G (summarized in Figure 1), the appropriate Karplus equation which we denote as an analogue of solvolyis.\(^{15} \) This is pictured by pathway ii in which positive charge is localized on the atom which charge is localized. It is reasonable to suppose that if the partition among isomeric ion–neutral complexes depends upon the conformations of the parent ions, then the \( M^+ \) and \( MH^+ \) ions ought to give comparable branching ratios.

The EBBFlow data argue that the epfluoruronium ion \( 1a \) is a bona fide intermediate within ion–neutral complexes. Ionization of \( \beta\text{-fluorophenyl-d}_2 \) phenyl ethers \( 8a \) and \( 8c \) in the gas phase yields the neutral products represented in eq 5. Cationized alkyl phenyl ethers decompose in the gas phase by a process that has been described as an analogue of solvolyisis.\(^{43,45} \) This is pictured by pathways i and ii in eq 5, which proceed via intermediate ion–neutral complexes.

Usually this mechanism predominates over the direct \( \beta \)-elimination represented by pathway ii. The final products from the ion–neutral complexes result from Brensted acid–base reactions, set), the dihedral angles differ by less than 5%, and the coefficients for the cos \( \phi \) terms based on the 6-31G* geometry (8.2 Hz for acute angles and 9.4 Hz for obtuse) do not differ greatly from those in eq 4. Using the dihedral angles for \( 8 \) summarized in Figure 1, we calculate that the vicinal coupling constants for the anti conformer of \( 8a \) ought to be \( |J| = 2.2 \text{ and } 10.3 \text{ Hz} \), while the vicinal coupling constants for a gauche conformer should be \( |J| = 6.8 \text{ and } 0.5 \text{ Hz} \). From the observed vicinal coupling constants, we have two independent determinations of the mole fraction of gauche: 0.804 and 0.836. The agreement between these two values ratifies our use of SCF-determined dihedral angles and confirms that the anti conformer is less stable than the gauche (experimental \( \Delta G^\circ = 2.5 \text{ kJ mol}^{-1} \) in chloroform solution). This may be compared with the experimental preference for gauche reported in the case of 1,2-difluoroethane, for which higher level ab initio computations favor the anti conformation (SCF calculations with even smaller basis sets give a FCC dihedral angle close to the value of 74° extracted from the microwave spectrum). \(^{18} \) The conjugate acid MH\(^+\) for \( M = 8 \) is calculated to have gauche conformers lower in energy than its anti conformers. Likewise, semiempirical calculations (AM1) predict that the radical cation \( 8^* \) also favors the gauche conformers (as would be anticipated on the basis of the expectation that the C–F dipole will point toward the atom on which positive charge is localized). It is reasonable to suppose that if the partition among isomeric ion–neutral complexes depends upon the conformations of the parent ions, then the \( M^+ \) and \( MH^+ \) ions ought to give comparable branching ratios.

The EBBFlow data argue that the epfluoruronium ion \( 1a \) is a bona fide intermediate within ion–neutral complexes. Ionization of \( \beta\text{-fluorophenyl-d}_2 \) phenyl ethers \( 8a \) and \( 8c \) in the gas phase yields the neutral products represented in eq 5. Cationized alkyl phenyl ethers decompose in the gas phase by a process that has been described as an analogue of solvolyisis.\(^{43,45} \) This is pictured by pathways i and ii in eq 5, which proceed via intermediate ion–neutral complexes.

Figure 1. SCF-optimized geometries (3-21G) of 2-fluoroethanol, anti and gauche 8, and one conformer of the conjugate acid of 8.

between the charged and neutral partners to yield phenol molecular ions and neutral fluoroethylene, as portrayed by the second step of eq 5. The $^{19}$F NMR spectra (H-decoupled) of the labeled fluoroethylenes from ionization of 8b and 8c in the electron bombardment flow (EBFlow) reactor are reproduced in Figure 2, and the proportions of the isotopomers of fluoroethylene are summarized in Table I.

Neutral product studies also give results consistent with fluorine transposition in free ions. Electron bombardment of a mixture of BrCH$_2$CD$_2$F and tert-butyl chloride in the EBFlow yields 1-chloro-1-fluoroethanes as the predominant products from the gaseous fluoroethyl cations. These recovered neutrals are produced by chloride abstraction from tert-butyl chloride (analogous to fluoroethylene reactions previously reported from tert-butyl fluoride$^{8b}$), as eq 6 depicts. Both $d_2$ isomers are recovered (in an approximate ratio of 9a:9b = 2:1). This means that if fluorine bridging takes place, the epifluoronium ion isomerizes via eq 1 (just like the ions discussed in ref 6) prior to its neutralization by chloride abstraction.

Discussion

Gaseous molecular ions derived from 8 decompose via ion-neutral complexes, some of which contain epifluoronium ions (1a), which are deprotonated before they have a chance to rearrange to 2a. The comparison summarized in eq 3 bears out one of the predictions for a complex-mediated mechanism: namely that radical cations and conjugate acid ions yield nearly the same ratios of C$_6$H$_5$DO$^+$ from the radical ion of phenol are close, this is consistent with the expectation that the observed branching ratios do not depend on whether the parent ion is an odd-electron or an even-electron species. The mass spectrometric data confirm our interpretation that the neutral products collected in the EBFlow reflect the fluoroethyl cations formed in the intermediate ion-neutral complexes. Field ionization-CAD studies have shown that the C$_6$H$_5$O$^+$ fragment from the radical ion of 8c has exclusively the structure phenol$^*$. It is likely that the C$_6$H$_5$DO$^+$ fragment has the structure PhOD$^+$ and that the corresponding fragments from 8b also have exclusively phenolic structures.

The distribution of recovered neutral products in the EBFlow agrees well with the ratio of PhOH$^+$ to PhOD$^+$ observed in the electron impact mass spectra of 8b and 8c.$^{16}$ Three important features warrant emphasis: (1) A major product (CHF$^+$=CD$_2$F from 8b, CDF$^+$=CH$_3$ from 8c) results from transposition of fluorine. (2) A major product (CDF$^+$=CH$_3$F from 8b, CHF$^+$=CDF from 8c) results from transposition of hydrogen. (3) No product is observed in which hydrogen and fluorine have both transposed (CHF$^+$=CHD from 8b, CDF$^+$=CHD from 8c).

A simple calculation of branching ratios and isotope effects leads to the conclusion that, for the radical ions of 8, the competition between pathways i and ii in eq 5 corresponds to the branching ratios $i/i$ = 1.2 ± 0.2 for 8b and $i/i$ = 2.4 ± 0.5 for 8c. This is based on an analysis of the data in Table I after correction for extraneous C$_2$H$_5$=CHF in the neutral product from 8c. The proportions of neutral products from 8b correspond to a PhOD$^+/PhOH^+$ ratio within experimental error of the value seen in the mass spectrum (cf. eq 3a), and we analyze the product distribution as shown in Scheme I. However, the mixture of fluoroethylenes from 8c corresponds to a PhOD$^+/PhOH^+$ yield approximately 2 times greater than what is seen in the mass spectrum. We attribute this to side reactions that yield vicinal elimination.

other proton transfers from unhindered carbocations have been only four experimental product ratios (excluding the of pathway iii (Le. iii/i for the values for the undeuterated analogue which do not produce PhOH‘, and we correct the neutral product yield as summarized in Scheme II so that it agrees with the mass spectrometric measurement. Such vicinal elimination appears to play a much smaller role in 8b, presumably because it is suppressed by a large primary deuterium isotope effect.

The data are analyzed in terms of Schemes I and II. There are two branching ratios and four deuterium isotope effects, but only four experimental product ratios (excluding the E/Z ratios, which equal 1.0 but are not germane) are available. We assume that the second step of pathway i has an isotope effect in the domain 1.0 ≤ kH/kD ≤ 1.6 (the range in which the values for all other proton transfers from unhindered carbocations have been found to lie(22)) and that the second step of pathway ii has a primary isotope effect, kH/kD, within the same domain (and a negligible secondary isotope effect). If we consider the mole fractions X and Y of pathways i and ii from 8b·+, respectively, and the corresponding mole fractions V and W from 8c·+, we arrive at the algebraic expressions shown in Schemes I and II. The values of X and V turn out to be functions of kH/kD, while the values of Y and W are functions of kH/kD and kH/kD.

From the experimental data and the assumed domains of kH/kD and kH/kD, we get a range of values for the mole fractions corresponding to each pathway. The values of W/V and (1 - W - V)/V are the branching ratios i/i and i/i, respectively. If we assume that there must be a normal isotope effect on pathway iii (i.e. iii/i for 8b is not greater than iii/i for 8c·+), this implies further constraints on the allowable solutions for Schemes I and II (for instance, it does not permit the isotope effects to exceed the upper bound that we have imposed). We compute the proportions of the competing pathways to be 40 ± 4% i, 48 ± 3% ii, and 9 ± 5% iii for 8b and 26.5 ± 3% i, 63 ± 6% ii, and 13.5 ± 6% iii for 8c. (The percentages do not sum exactly to 100% because of the manner in which the uncertainties overlap.) The proportions for 8c·+ are probably not much different from the values for the undeuterated analogue 8a·+, since this represents a competition among fluoride bridging, hydride shift, and vicinal elimination in which the secondary isotope effects may be comparable.

The experimental data imply that transposition of fluorine and hydrogen are competing and not sequential events. They rule out a transposition of fluorine in the molecular ion (which had been proposed elsewhere(23) prior to the shift of hydrogen. If such an isomerization of 8·+ had occurred, then we should have seen products from a subsequent hydrogen shift, which would have corresponded to sequential F- and H-transposition. Because no products of sequential shift are observed, the molecular ions cannot be rearranging their labels while maintaining (or reverting to) covalent structures corresponding to 8·+. In our view, the results can be accommodated only by a mechanism that includes cleavage of the sp3-carbon-oxygen bond with formation of bridged ion (which had elsewhere been considered and rejected for the facts that X = Cl and X = Br). The proportions of path i versus path ii in 8b show that deuteride shift is 1.2 times more probable than fluoride transposition. This is to be compared with results for the higher homologue CH3CDFCH2OPh·+(3·+), for which deuteride shift is 4 times more likely than fluoride transposition.

The occurrence of vicinal elimination (pathway iii) without any transposition invites comment. This is comparable to the proportion of vicinal elimination reported for 3·+ (=8%)(4). Because the partition among pathways i—ii must be nearly the same for MD·+ ions as for M·+ (since the EI and CI mass spectra show nearly the same proportions of C2H2DF and C2HD2F loss), vicinal elimination cannot be occurring via a distonic intermediate (which is a pathway unique to radical cations. An alternative possibility is for elimination without transposition to occur via a hydrogen-bonded complex that forms in competition with ion-neutral complexes. Such a possibility is consistent with a suggestion by Audier et al. in their interpretation of the MIKES of sec-alkyl phenyl ether molecular ions.23 The corresponding intermediates from 8 might be represented as [PhOH·+-CH2=CHF] derived from 8a·+ and [PhOH·+-CH2=CHF] for the MD·+ ion from 8a. The species in brackets are intended to portray local minima on the potential energy surface and are not meant to imply that these possess static structures.

In principle, the ion-neutral complexes depicted in eq 5 could be transition states leading to hydrogen-bonded complexes. In the case of the next higher homologue, such an interpretation can be ruled out. The complexes derived from 3 (represented schematically in eq 2) interconvert via hydride shifts prior to expulsion of phenol·+, implying that they must have nonzero lifetimes. However, for the cations derived from 8, the experimental evidence rules out interconversion of the complexes. On the one hand, this implies (strictly speaking) that pathway i either passes through a discrete intermediate (1a PhO·+), as drawn in eq 5) or else corresponds to a transition state on route to structures that cannot subsequently decompose via [2a PhO·+] (pathway ii). On the other hand, since free fluoroethyl cations assume the structure 2a, as revealed by eq 6, we may confidently conclude that 1a does indeed convert to 2a on the microsecond time scale. Species that decompose much faster than the 1a → 2a isomerization, such as ion-neutral complexes containing 1a, ought nevertheless to have nonzero lifetimes. Otherwise we would have expected to recover the neutral fluoroethanes that result from hydride shift subsequent to fluoride shift (which are conspicuously absent in the data reproduced in Figure 2).

Conclusion

The long-sought epifluoronium ion (1a) has been found to correspond to a stable structure. Neutral product studies of gaseous ion-neutral complexes show that fluorne transposition and hydrogen transposition in cationic precursors containing FCH2CH2 groups are competing pathways. The absence of any products from sequential rearrangements suggests that the two pathways produce distinct, noninterconverting intermediates, which

Characterization of Iron–Sulfur Cubane Clusters by Fast Atom Bombardment Mass Spectrometry: The Formation of Ionic \([\text{Fe}_m\text{S}_n]^\text{+}\) Clusters through Gas-Phase Unimolecular Reduction Processes and Their Solution Parallels

Wen-Lian Lee,¹ Douglas A. Gage,¹b Zhi-Heng Huang,¹b Chi K. Chang,¹,¹a Mercouri G. Kanatzidis,*¹,¹a and John Allison¹,¹a

Introduction

Proteins containing iron–sulfur clusters frequently serve as redox enzymes and participate in electron-transfer reactions associated with processes such as photosynthesis, nitrite reduction, and nitrogen fixation.⁴ At present, four distinct types of Fe–S cluster cores, in various oxidation states, have been identified in such enzymes: Fe₄S₄, Fe₃S₄, Fe₂S₄, and FeSₓ. The iron centers in these clusters form bridges in proteins, usually by bonding to sulfur atoms of cysteine residues. Most of these clusters participate in one-electron redox processes.⁴ They frequently contain iron atoms in one or more oxidation states, usually Fe⁰ and Fe⁺. A variety of iron/sulfur core oxidation states have been established for the various FeS₄ clusters present in proteins. Those identified to date include the following: \([\text{FeS}_4]^{2-}\), \([\text{FeS}_4]^{10+}\), and \([\text{FeS}_4]^{12+}\).

In view of the diversity of structures and biological functions, these complexes are difficult to characterize by direct studies of the proteins themselves. Fortunately, synthetic analogs of the mono-, bi-, and tetrairon centers have been developed to provide insights into their intrinsic properties in the absence of protein-imposed constraints. Of the structurally characterized synthetic models for the various \([\text{Fe}_m\text{S}_n]\) clusters now available, the cubane-type, \([\text{Fe}_4\text{S}_4]\), core geometry appears to be the most commonly encountered, and it has been the focus of an intensive body of structural, spectroscopic, and magnetic studies for the last two decades.⁵ ⁶ A wide variety of model complexes of the type \([\text{Fe}_4\text{S}_4]^\text{+}\) have been made in which the anionic components, \(X^\text{-}\), are a variety of thiolates (SR⁻), halides (Cl⁻, Br⁻, and I⁻),³⁴ and alkoxides (OR⁻),² as well as combinations of these ligands.¹⁰

Abstract: Fast atom bombardment mass spectrometry (FAB-MS) has been used to analyze a series of iron–sulfur clusters (A)\text{Fe}_m\text{S}_nX_n, where A = R, N or Ph, P and X = Cl, Br, SEt, SPh. A cluster with mixed Cl, SPh ligands was also studied. The usefulness of the FAB technique in characterizing these and related biologically-relevant complexes is evaluated. The best FAB-MS results for these clusters were obtained with 3-nitrobenzyl alcohol (NBA) and 2-nitrophenyl octyl ether (NPOE) as matrices. The most unique feature of the negative ion FAB mass spectra is the identification of the intact ionic core \([\text{Fe}_4\text{S}_4]^{2-}\), as well as structural elucidation of preformed anions \([A]^{(A)}\text{Fe}_4\text{S}_4X_4^{2-}\), and a series of cluster fragment ions. A mechanism is proposed to explain the formation of small \([\text{Fe}_4\text{S}_4]\) clusters through unimolecular reduction processes that involve only +2 and +3 oxidation states for the Fe atoms. This work demonstrates that FAB-MS can be employed as a valid method for rapid molecular weight determination as well as structural elucidation of \([\text{Fe}_4\text{S}_4]\) cluster-containing complexes.