Formation and Reactivity of Gaseous Iron-Sulfur Clusters

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Dedicated to Professor Heinz Georg Wagner on the occasion of his 75th birthday

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The gas-phase reactions of Fe_n^+ clusters, $n = 1–6$, with COS and CS_2 have been investigated by means of Fourier-transform ion-cyclotron resonance mass spectrometry. Whereas CS_2 predominantly substitutes one Fe atom, COS exclusively affords multiple sulfur transfer and thus opens a synthetic route to gaseous $Fe_nS_x^+$ clusters. In the final products such as $Fe_2S_2^+$, $Fe_3S_2^+$, and $Fe_4S_4^+$, the sulfur atoms appear to occupy multiple coordination sites much like in the analogous biogeneous iron-sulfur clusters. Bracketing experiments find $IE(Fe_2S_2) = 7.2\pm0.3$ eV besides providing upper limits for $IE(Fe_3S_2)$ and $IE(Fe_4S_4)$. In accordance with the low $IE(Fe_2S_2)$, $Fe_2S_2^+$ does not activate H_2 or small hydrocarbons and only exhibits rather limited reactivity towards more reactive substrates.

Introduction

Among the many functions of iron in biological systems, its involvement in redox processes is particularly important. Inter alia, electron-transfer (ET) reactions associated with photosynthesis, respiration, and nitrogen fixation rely heavily upon this transition metal. A common feature of the different enzymes mediating these processes is that their catalytically active centers are not comprised of a single iron atom but consist of several Fe atoms bound to sulfur.[1–4] The [4Fe-4S] core with its hetero-cubane structure is an especially famous example of such clusters.

Various strategies have been pursued in order to elucidate the chemical relationship between the remarkable structures of the iron-sulfur clusters and their outstanding reactivity in terms of ET. To probe the intrinsic properties of these systems, exclusion of environmental effects is warranted. This approach can be rigorously achieved by gas-phase techniques that allow a thorough investigation of the object of interest. For instance, anionic clusters of the type $Fe_nS_x^-$ have been examined by means of photoelectron spectroscopy.[5,6] In the case of their cationic counterparts, however, experiments so far have mainly centered around mononuclear systems FeS_x^+.[6–12] In a joint study with the group of Armentrout, we have recently derived thermochemical data with respect to polynuclear clusters $Fe_nS_x^+$, $n \leq 5$ and $x \leq 2$, from the kinetic energy dependences of the reactions of Fe_n^+ with COS and CS_2.[13] Although these studies provide evidence for multiple sulfur transfer, the guided-ion beam (GIB) technique applied is not the method of choice for the detailed investigation of such processes. Instead, the longer time-scale of Fourier-transform ion-cyclotron resonance mass spectrometry (FT-ICR MS) and its supreme suitability for MS^n experiments make this technique particularly adequate for the elucidation of multi-step reactions. Since it cannot compete with the GIB approach for the determination of thermochemical quantities, however, both methods are complementary. Taking advantage of this situation, the present FT-ICR study focuses on the primary and consecutive reactions between Fe_n^+ clusters, $n \leq 6$, with COS as well as CS_2. Particular attention has been paid to possible structural assignments of the evolving $Fe_nS_x^+$ ions. Moreover, the reactivity of the cluster ions $Fe_2S_2^+$, $Fe_3S_2^+$, and $Fe_4S_4^+$ has been explored briefly, with an emphasis on ET reactions and a comparison with the analogous iron-oxide clusters.

Results

Reactions with COS and CS_2

The reactions of Fe_n^+ with COS lead to stepwise sulfur transfer to the metal cluster, as shown in the reaction according to Equation (1).

$$Fe_n^+ + x\,COS \rightarrow Fe_nS^+ + CO + (x-1)\,COS \rightarrow\rightarrow Fe_nS_x^+ + x\,CO \tag{1}$$

As was established previously, mononuclear iron only accepts a single sulfur atom with an appreciable efficiency.[10] In contrast, the second sulfur transfer for Fe_2^+ is significantly faster than the first and no further reaction can be observed. Similarly, the reaction apparently stops after transfer of two S atoms in the case of Fe_3^+. For $n =$

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4 and 6, addition of four S atoms occurs whereas even $x = 5$ is reached for Fe_5^+. Although the maximum sulfur contents observed do not necessarily correspond to the ultimate level at infinite reaction times, they nevertheless imply that any possible further reactions proceed significantly less efficiently.

A more detailed analysis required a quantitative treatment. To this end, the experimental temporal ion abundances were fitted to the kinetic model defined by reaction (1). Note that the validity of this model, postulating a stepwise sulfur transfer, can safely be assumed because no termolecular reactions are feasible at the low pressures maintained. However, a minor complication arose from side reactions with contaminants in the cases of Fe_4^+ and Fe_5^+. In order to monitor the whole series of consecutive processes, reaction times up to 30 s were necessary. Thus, continuous reactions with background oxygen and water led to the accumulation of products formed by oxidative cluster degradation and hydrolysis (for $n = 4$, species such as $Fe_2O_2^+$, $Fe_3S_2^+$, and $Fe_4S_2O^+$ are indicative of such processes). To a first approximation, similar degradation or hydrolysis probabilities may be assumed for all intermediates $Fe_nS_x^+$ within a reaction series such that the neglect of the by-products should not affect the rate constants derived for the sulfur-transfer reactions themselves. Given the relatively low amounts of the by-products resulting from contamination ($\leq$ 30% and 15% of the total ion intensity for $n = 4$ and 5, respectively), this approach indeed appears reasonable.

The results of the kinetic modeling show uniformly high efficiencies for the reactions of the clusters with $n \geq 3$ (Table 1). In these cases, the operation of substantial enthalpic or kinetic restrictions can obviously be excluded. This finding suggests lower limits for the binding energies of the iron-sulfur clusters according to $D_{298}(Fe_nS_{x-1}^+{-}S) \geq D_{298}(OC{-}S) = 308\ kJ{\cdot}mol^{-1}$, $n = 3-6$.[14]

The reactions of Fe_n^+ with CS_2 do not afford efficient sulfur transfer but are included in the present work for comparison with the GIB data. Mononuclear Fe^+ does not react with CS_2 at thermal energies.[10,11] Similarly, the reaction of Fe_2^+ exhibits a low efficiency of $\varphi = 0.01$ with simple adduct formation as the main reaction (80% branching ratio, b.r.). Doubling of the pressure (from 1 to $2{\cdot}10^{-7}$ mbar) does not change the rate constant for this process within the relative uncertainty of 10% such that irradiative rather than termolecular stabilization seems to account for the association.[15] A second reaction channel yields $Fe_2S_2^+$ (10% b.r.). Presumably, this process involves Fe_2S^+ as an intermediate that does not build up in substantial concentrations because of a rapid second sulfur transfer. See reaction in Equation (2) with $n = 2$.

$$Fe_n^+ + 2\,CS_2 \rightarrow Fe_nS^+ + CS + CS_2 \rightarrow Fe_nS_2^+ + 2\,CS \qquad (2)$$

The occurrence of CS_2^+ as a third product (10% b.r.) might point to the presence of residual amounts of electronically excited Fe_2^+ because charge transfer from ground-state Fe_2^+ to CS_2 would be strongly endothermic [$IE(Fe_2) = 6.30 \pm 0.01$ vs. $IE(CS_2) = 10.07 \pm 0.01$ eV).[16,17] Note, however, that the reaction of Fe_2^+ with CS_2 is the only case where there is a possible indication of the involvement of electronically excited states. Moreover, for the presence of large amounts of excited Fe_n^+ one would not expect the observed exponential decrease of the reactant Fe_n^+ ions as is evident from linear slopes in semi-logarithmic plots. Therefore, the formation of CS_2^+ in the reaction of Fe_2^+ is rather ascribed to the presence of small amounts of an unobserved reactive intermediate. Because of the low efficiency of this reaction channel ($\varphi = 10^{-3}$), involvement of a contaminant such as O_2 cannot be excluded either.[18]

The larger clusters react much more efficiently with CS_2 ($\varphi = 0.5-0.8$). Here, the main process corresponds to substitution of one Fe atom by CS_2 [Equation (3)]. Only for Fe_3^+, reaction (2) still takes place (25% b.r.). Obviously, CS_2 binds quite strongly to the larger Fe_n^+ clusters.

$$Fe_n^+ + CS_2 \rightarrow Fe_{n-1}CS_2^+ + Fe \qquad (3)$$

The same conclusion can be drawn from the consecutive reactions that efficiently lead to the mere association of one or even two further CS_2 molecules for $n \geq 4$. Since the pressures applied for the larger cluster ions were more than an order of magnitude lower than in the case of Fe_2^+, the tendency towards termolecular stabilization should be even more reduced and, therefore, cannot account for the effective relaxation. Instead, a deep potential well of the ion-molecule complex is supposed to increase the lifetime of the collision complexes, thereby facilitating their relaxation. In comparison with Fe_2^+, the higher numbers of internal degrees of freedom in the $Fe_{n-1}CS_2^+$ clusters, $n = 4-6$, also allow a faster redistribution of the energy released upon complexation and thereby raise the lifetimes of the energetic encounter complexes as well. Such phenomena are quite

Table 1. Bimolecular rate constants k and efficiencies for the reactions of Fe_n^+ with COS derived from kinetic modeling

Reaction		$k/10^{-10}$ cm^3 s^{-1} (φ)					
	$n =$	1	2	3	4	5	6
$Fe_n^+ + COS \rightarrow Fe_nS^+ + CO$		2.4[a] (0.19)	0.35 (0.032)	6.8 (0.67)	7.6 (0.77)	7.6 (0.79)	4.2 (0.44)
$Fe_nS^+ + COS \rightarrow Fe_nS_2^+ + CO$			6.8[b] (0.66)	7.9[b] (0.79)	6.4 (0.66)	7.5 (0.79)	7.4 (0.79)
$Fe_nS_2^+ + COS \rightarrow Fe_nS_3^+ + CO$					8.9 (0.93)	8.4 (0.89)	8.0 (0.86)
$Fe_nS_3^+ + COS \rightarrow Fe_nS_4^+ + CO$					6.7[b] (0.71)	7.1 (0.76)	7.1[b] (0.76)
$Fe_nS_4^+ + COS \rightarrow Fe_nS_5^+ + CO$						6.6[b] (0.71)	

[a] For the slow transfer of a second S atom and further consecutive reactions, compare: I. Kretzschmar, *Energetics and Reactivity of the Binary Transition-Metal Sulfides of the 3rd and the 4th Row*; Shaker: Aachen, **1999**. [b] Upper limits of $k < 5{\cdot}10^{-11}$ cm$^3{\cdot}$s^{-1} for a further S atom transfer can be inferred from consideration of the signal-to-noise ratios.

common for the reactions of cluster ions in the highly diluted gas phase.[19]

Reactivity of $Fe_2S_2^+$

The reactivity of the smallest iron-sulfur cluster, i.e. $Fe_2S_2^+$, was investigated in some detail. Focusing on this cluster is advantageous for practical reasons because it can easily be generated in high abundance. Moreover, a comparison with the analogous $Fe_nO_x^+$ ions promised to be most revealing for the dinuclear systems because $Fe_2O_2^+$ has been studied extensively.[20,21]

$Fe_2S_2^+$ does not react with the inorganic substrates H_2, N_2, O_2, CO, CO_2, and H_2O ($\varphi < 10^{-3}$). Upon exposure to NH_3, $Fe_2S_2^+$ slowly binds up to three molecules of the neutral reagent. The determined rate constant $k = 3.8 \cdot 10^{-11}$ $cm^3 \cdot s^{-1}$ ($\varphi = 0.019$) does not show any dependence on the pressure [$p(NH_3)$ between 1 and $3 \cdot 10^{-7}$ mbar], thus again suggesting radiative rather than termolecular relaxation of the association complexes. Compared with H_2O, the enhanced reactivity of NH_3 reflects its higher basicity that leads to a stronger dative binding which in turn raises the lifetime of the energetic ion-molecule complexes, see above. Similarly, Nakajima et al. found association of NH_3 to be much more efficient than H_2O addition for larger $Fe_nS_x^+$ clusters. However, a comparison with these data should take into account that they refer to differently produced clusters such that the structural identities of the $Fe_nS_x^+$ species are not necessarily given.[6]

In view of the low reactivity of $Fe_2S_2^+$ towards inorganic molecules, one also does not expect it to readily activate hydrocarbons. Therefore, the reactions of $Fe_2S_2^+$ with alkanes were not investigated but its reactivity toward alkenes was addressed right away. Whereas exposure to 1-butene only afforded rather slow adduct formation ($\varphi = 0.04$), 1,4-cyclohexadiene was efficiently activated by $Fe_2S_2^+$ ($k = 6.3 \cdot 10^{-10}$ $cm^3 \cdot s^{-1}$, $\varphi = 0.61$). The reactivity of 1,4-cyclohexadiene is governed by its tendency towards H_2 elimination which meets expectation because the presumably concomitant formation of benzene provides a strong thermodynamic driving-force for this process. Consequently, loss of C_6H_6 constitutes the main reaction channel [reaction (4), 80% b.r.]. Note that this process corresponds to a formal reduction of the iron cluster-core. The second reaction channel (20%) results in hydro-desulfuration[22] [reaction (5)] and thus highlights the redox character of the reactions in an even more pronounced manner. It remains unclear whether the ionic product contains an intact benzene molecule or if further bond activation involving the remaining S atom has occurred.

$$Fe_2S_2^+ + C_6H_8 \rightarrow [Fe_2,S_2,H_2]^+ + C_6H_6 \qquad (4)$$

$$Fe_2S_2^+ + C_6H_8 \rightarrow [Fe_2,S,C_6,H_6]^+ + H_2S \qquad (5)$$

The primary products undergo efficient consecutive reactions. Whereas both $[Fe_2,S,C_6,H_6]^+$ and $[Fe_2,S_2,H_2]^+$ add one more 1,4-cyclohexadiene molecule under dehydrogenation [reactions (6) and (7)], the latter also loses two molecules of H_2 upon reaction with C_6H_8 [reaction (8), 70% b.r.]. Formally, this process regenerates the $Fe_2S_2^+$ cluster core with one added benzene ligand and thus corresponds to the reverse of the reduction in reaction 4. Apparently, the dinuclear cluster can easily switch from one oxidation state to another.

$$[Fe_2,S,C_6,H_6]^+ + C_6H_8 \rightarrow [Fe_2,S,C_{12},H_{12}]^+ + H_2 \qquad (6)$$

$$[Fe_2,S_2,H_2]^+ + C_6H_8 \rightarrow [Fe_2,S_2,C_6,H_8]^+ + H_2 \qquad (7)$$

$$[Fe_2,S_2,H_2]^+ + C_6H_8 \rightarrow [Fe_2,S_2,C_6,H_6]^+ + 2\,H_2 \qquad (8)$$

ET Reactions

Given the well-known activity of biogeneous Fe_nS_x clusters in terms of ET, the respective behavior of their gaseous counterparts also deserves attention. Although the reactivity observed for $Fe_2S_2^+$ already provides some first indications with regard to its redox activity, further efforts are necessary to address this issue explicitly. Within FT-ICR mass spectrometry, a straightforward determination of *IE*s can be achieved by bracketing experiments. To this end, the ion of interest A^+ is exposed to substrates B with known *IE*s. Occurrence of ET indicates $IE(A) \geq IE(B)$, whereas in the absence of ET, the opposite relation should hold true as long as no kinetic barriers are associated with the ET process. The latter assumption is valid if the structure of the substrate B is not strongly changed upon ionization, i.e., in the case of favorable Franck−Condon factors that are usually observed for (substituted) arenes.

The bracketing method can be refined by consideration of the efficiency of the ET process instead of the only qualitative distinction between occurrence and non-occurrence.[23] In the present case, however, major difficulties arose from the apparently rather low *IE*s of the Fe_nS_x clusters. In order to observe ET, substrates with similarly small *IE*s such as amino- or methoxy-substituted arenes were required. The low vapor pressures and the unfavorable pumping characteristics of these compounds severely complicate their handling in high-vacuum devices and prevent the determination of accurate absolute rate constants. Moreover, the appreciable basicity of aniline and its derivatives results in strong interactions between these reagents and the ionic clusters, thereby favoring mere association compared with ET. For larger clusters, adduct formation becomes even more important because of lifetime effects (see above) such that ET may no longer compete although it is still feasible thermochemically. Hence, the investigations with regard to ET had to be restricted to the smaller clusters $Fe_2S_2^+$, $Fe_3S_2^+$, and $Fe_4S_4^+$. Instead of the impractical measurement of absolute rate constants, the ratio between the rates of ET and adduct formation, as evidenced from the product distribution, was considered. For the stepwise decrease of the substrates' *IE*s, one expects the ratio k_{ET}/k_{add} to rise steeply from its low background level as soon as the *IE* of the substrate matches that of the Fe_nS_x cluster and the ET process becomes thermodynamically accessible. Indeed, this situation was found in the case of $Fe_2S_2^+$ where k_{ET}/k_{add} increases by more than one order of magnitude when changing the substrate from 1,4-dimethoxybenzene (IE = 7.56 eV)[17] to N-methylaniline (IE = 7.32 eV)[17] and then to N,N-dimethylaniline (IE = 7.12 eV, Figure 1).[17] This progression roughly suggests $IE(Fe_2S_2)$ = 7.2±0.3 eV. In the reaction with N,N-dimethylaniline, hydride transfer from the substrate to the $Fe_2S_2^+$ cluster occurs with approximately equal efficiency as ET [reaction (9)]. Like reaction (4) with 1,4-cyclohexadiene, this process demonstrates the ready uptake of two reduction equivalents by $Fe_2S_2^+$. Similarly, the hydro-desulfuration observed with N-methylaniline [reaction (10)] has its counterpart in reaction (5) for $Fe_2S_2^+$ with 1,4-cyclohexadiene.

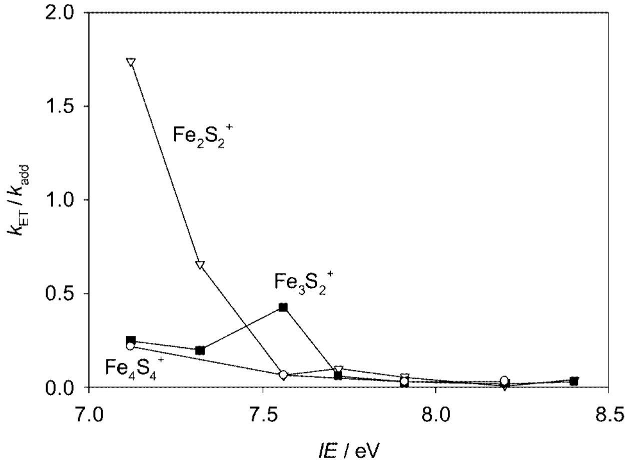


Figure 1. Ratio of ET versus addition processes for the reactions of $Fe_nS_x^+$ clusters with several substrates, B, as a function of IE(B). Specifically, the substrates applied were (in the order of increasing IE): N,N-dimethylaniline, N-methylaniline, 1,4-dimethoxybenzene, aniline, 2-methylnaphthalene, anisole, and mesitylene.

$$Fe_2S_2^+ + C_6H_5N(CH_3)_2 \rightarrow C_6H_5N(CH_3)CH_2^+ + [Fe_2,S_2,H] \quad (9)$$

$$Fe_2S_2^+ + C_6H_5NHCH_3 \rightarrow [Fe_2,S,C_7,H_7,N]^+ + H_2S \quad (10)$$

In the case of $Fe_3S_2^+$, the situation is more complex. The ratio k_{ET}/k_{add} substantially increases for the change from aniline (IE = 7.72 eV)[17] to 1,4-dimethoxybenzene (IE = 7.56 eV),[17] but drops again for N-methylaniline (IE = 7.32 eV).[17] This non-monotonic behavior might possibly result from differences between the substrates' tendencies towards adduct formation. Considering the ratio k_{ET}/k_{add} rather than the absolute rate constant k_{ET} as a criterion for ET relies on the assumption that k_{add} does not strongly change for the differently substituted arenes. However, it cannot be excluded that the small differences between the various substrates already give rise to significantly distinct lifetime effects that might account for the non-monotonic progression of k_{ET}/k_{add}. Nonetheless, it is not clear why the reaction between 1,4-dimethoxybenzene and $Fe_2S_2^+$ does not exhibit a similar anomaly.

For $Fe_4S_4^+$, low k_{ET}/k_{add} ratios were observed without exception. From the present experiments, one cannot judge whether this finding merely reflects a higher tendency towards association for the larger cluster or if a further decrease of the substrates' IEs were necessary to induce efficient ET. Note that probing the latter is far from trivial because of the low vapor pressures of the respective compounds. Hence, only upper limits for the IEs of Fe_3S_2 and Fe_4S_4 can be derived for the time being: $IE(Fe_3S_2) \leq 7.6$ and $IE(Fe_4S_4) \leq 7.6$ eV.

Discussion

Comparison between FT-ICR and GIB Data

First, the present results regarding the reactivity of Fe_n^+ clusters toward COS and CS_2 are compared with the previous GIB data.[13] With regard to the reactions with COS, both methods find sulfur transfer according to reaction (1) as the exclusive process taking place at thermal energies. Whereas the primary reactions are quite efficient for clusters sizes $n \geq 3$, a significantly decreased reactivity is consistently observed in the case of Fe_2^+ (Table 1). Since this reaction is strongly exothermic ($\Delta_r H^\circ = -104\pm5$ kJ·mol^{-1}),[13] kinetic rather than energetic restrictions must account for its low efficiency. A possible explanation suggested previously centers on the formally forbidden spin-inversion associated with the dissociation of COS ($^1\Sigma$ ground state) into CO ($^1\Sigma$) and S (^3P).[11,13,24] For the larger metal clusters, the presence of numerous energetically accessible electronic states mixing with the wave functions of COS is likely to weaken this restriction. In the case of the dinuclear system, however, the smaller number of electronic states appears to be insufficient for suspending spin selection-rules. This line of argument is supported by the high efficiency ($\varphi = 0.66$) observed for the consecutive reaction of Fe_2S^+ with a further COS molecule. Apparently, symmetry breaking by the sulfide ligand effectively releases spin restrictions. In addition, occurrence of the consecutive reactions for $n \geq 2$ implies negative reaction enthalpies associated with these processes. These conclusions are in full agreement with the thermochemical data derived for $Fe_2S_2^+$ and $Fe_3S_2^+$ from the GIB experiments.[13]

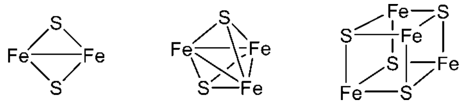
The agreement between the FT-ICR and GIB data also continues for the reactions of Fe_n^+ with CS_2. Here, substitution of one iron atom by CS_2 is the predominant process for $n \geq 3$ [reaction (2)] and largely suppresses sulfur transfer despite its thermochemical feasibility. In comparison with COS, the stronger binding of CS_2 presumably results from both its enhanced π-donor and π-acceptor properties. Similarly, CS is commonly known to bind to transition metals more strongly than CO.[25] Again, Fe_2^+ behaves differently from the larger clusters and does not undergo reaction 2 as both the FT-ICR and GIB approach demonstrate.[13] The CS_2 ligand probably interacts with more than one iron center such that expulsion of the second Fe atom is disfavored and instead the adduct $Fe_2CS_2^+$ is formed for $n = 2$. A further comment is also warranted with respect to reaction (2). Whereas the first sulfur transfer from CS_2 to Fe_2^+ is slightly endothermic ($\Delta_r H^\circ = 27\pm6$ kJ·mol^{-1}) according to the GIB method,[13] the observation of the consecutive

$Fe_2S_2^+$ product in the present work implies feasibility of the primary reaction under FT-ICR conditions. However, its low efficiency $\varphi = 10^{-3}$ also points to the operation of energetic or kinetic restrictions. On the basis of a simple Arrhenius approach, one finds an activation energy $E_A = -RT \ln\varphi = 17$ kJ·mol^{-1} which is in reasonable agreement with the $\Delta_rH°$ value determined by the GIB method.

Structural Assignments

A principal problem of mass-spectrometric studies results from the difficulty of structural assignments because these have to rely on indirect evidence only. In the case of the $Fe_nS_x^+$ clusters, previous studies primarily focused on the mononuclear FeS_x^+ ions.[8,10,12] Upon reaction with ethylene sulfide, Fe^+ adds to up to six sulfur atoms. Ligand-exchange, photodissociation, and collision-induced dissociation experiments point to the formation of S_2 or larger S_y units in these systems.[8] Similarly, FeS_2^+ generated from the reaction of Fe^+ with COS contains an S_2 ligand as well.[10] In contrast, the GIB study provided indications for separated S atoms in $Fe_2S_2^+$ and $Fe_3S_2^+$. In particular, the high bond-dissociation energies $D_0(SFe_n^+{-}S)$ and $D_0(Fe_n^+{-}S) > 400$ kJ·mol^{-1} derived for $n \geq 2$ suggest the occupation of multiple coordination sites by sulfur.[13] The interaction with more than a single metal center should saturate the open valencies of sulfur and thus diminish its tendency towards oligomerization.

The present findings further support the presence of separate S atoms in $Fe_2S_2^+$ and $Fe_3S_2^+$. Unlike FeS_2^+, they do not undergo ligand exchange with arenes as one would expect for $Fe_n(S_2)^+$ structures. The observed saturation at $x = 2$ in the reaction of Fe_2^+ with COS is consistent with rhombic $Fe_2S_2^+$ (Scheme 1). This geometry is also known for biogeneous [2Fe-2S] clusters.[1−4] In the case of $n = 3$, saturation after the addition of two S atoms is compatible with coordination to both faces of a triangle. Such a structure would correspond to the maximum number of binding interactions between each sulfur atom and the iron centers. For Fe_4^+, the metal cluster takes up four sulfur atoms that do not undergo exchange with arenes and therefore are not assumed to combine to form S_2 or even larger units. Given that the iron core in $Fe_4S_4^+$ adopts a tetrahedral structure as in the unperturbed Fe_4^+ system,[26] the maximum coordination possible would position each of the four S atoms above one triangular face. This geometry corresponds to the hetero-cubane structure known from biological systems.[1−4] In the cases of $n = 5$ and 6, the $Fe_5S_5^+$ and $Fe_6S_4^+$ clusters resulting from sulfur transfer were not exposed to further substrates such that the questions of ligand exchange and eventual sulfur oligomerization cannot be answered. However, in analogy to their smaller homologues, multifold coordination by separate sulfur atoms appears probable for these species. Similar conclusions have been drawn by Nakajima et al. for neutral Fe_nS_x clusters produced by laser vaporization of a solid iron-sulfur mixture.[6]



Scheme 1

Reactivity of $Fe_nS_x^+$ Clusters

The overall rather low reactivity found for $Fe_2S_2^+$ reflects the high thermochemical stability of this cluster as already inferred from the previous GIB experiments.[13] Presumably, the absence of hydrolysis and ammonolysis reactions results not only from the strength of the iron−sulfur bonds but also from the lower stability (in comparison with H_2O or NH_3) of H_2S which is the neutral by-product formed in hydrolysis or ammonolysis of $Fe_2S_2^+$. With regard to the reverse process, $Fe_2O_2^+$ indeed is known to react with two equivalents of H_2S to yield $Fe_2S_2^+$.[21] This observation indicates that hydrolysis of $Fe_2S_2^+$ is prohibited for thermochemical reasons. Compared with $Fe_2S_2^+$, the higher reactivity of $Fe_2O_2^+$ is also evident from its ability to attack non-activated hydrocarbons such as *n*-butane.[20,21] Obviously, the metal core cannot fully compensate for the electron deficiency of the O atoms such that the latter exhibit a high affinity for oxidation reactions. For $Fe_2S_2^+$, the lower electronegativity of sulfur leads to a better balanced electronic structure in this cluster and a significantly reduced oxidative power. The role of $Fe_2S_2^+$ as a mild oxidant becomes clearly visible in its reaction with 1,4-cyclohexadiene which apparently affords a reversible H_2 transfer. Moreover, this process points to the possibility of catalytic redox reactions of $Fe_2S_2^+$ which could be considered as gas-phase models for the active sites of the corresponding enyzmes.

The distinct behavior of $Fe_2S_2^+$ and $Fe_2O_2^+$ in terms of redox chemistry should also be reflected in the quantitative data derived for these systems. In comparison with $IE(Fe_2O_2) = 8.4 \pm 0.3$ eV,[21] $IE(Fe_2S_2) = 7.2 \pm 0.3$ eV is substantially lower, consistent with the arguments raised above. The present value obtained for $IE(Fe_2S_2)$ is somewhat larger than that inferred from the GIB approach, $IE_{GIB}(Fe_2S_2) = 6.64 \pm 0.35$ eV,[13] but both agree within the combined error margins. Note that one a priori might expect the present method to yield a slightly too high *IE* because the thermal energies of the reactants are not explicitly accounted for while they should decrease the energetic threshold of the ET reactions compared with those at $T = 0$ K. Nonetheless, the newly determined value indicates that the theoretical prediction $IE_{theo}(Fe_2S_2) = 7.76$ eV[27] does not lie as far from experiment as the comparison with $IE_{GIB}(Fe_2S_2)$ alone suggests. In the cases of Fe_3S_2 and Fe_4S_4, only upper limits could be derived for their *IE*s. Apparently, the *IE*s of these clusters are also quite low.

Conclusions

FT-ICR mass spectrometry has been used to study the formation and reactivity of cationic iron-sulfur clusters.

$Fe_nS_x^+$ clusters can be generated by the reaction of Fe_n^+ with COS whereas exposure of Fe_n^+ to CS_2 mainly leads to substitution of one Fe atom by CS_2. These findings are fully consistent with previous results obtained by means of guided-ion beam techniques.[13] For the final products of sulfur transfer such as $Fe_2S_2^+$, $Fe_3S_2^+$, and $Fe_4S_4^+$, the absence of ligand exchange provides evidence against the presence of S_2 or larger S_y units which have been proven in the case of mononuclear FeS_x^+. This difference can be rationalized by the involvement of multiple bridging bonds between the Fe core and the sulfur atoms that are only possible for the cluster ions. The interaction with more than a single metal center saturates the open valencies of the sulfur atoms thereby preventing oligomerization. Thus, the structures of the gaseous $Fe_nS_x^+$ ions appear to strongly resemble those of biogeneous iron-sulfur clusters.

Moreover, the formation of multifold bonds substantially stabilizes the $Fe_nS_x^+$ clusters and diminishes their reactivity as demonstrated for $Fe_2S_2^+$. The low reactivity of the latter becomes particularly evident in the comparison with the analogous oxide species $Fe_2O_2^+$. Thus, the lower electronegativity of sulfur results in a well-adjusted electronic balance for $Fe_2S_2^+$ such that it does not exhibit an increased tendency towards oxidation reactions. Hence, iron-sulfur clusters seem to be intrinsically well suited for the participation in reversible redox reactions and catalytic ET processes.

Experimental Section

Experiments were performed using a Spectrospin CMS 47X FT-ICR mass spectrometer[28,29] that has recently[30] been equipped with a Smalley-type[31] cluster-ion source developed by Bondybey, Niedner-Schatteburg, and co-workers.[32] Briefly, the fundamental of a pulsed Nd:YAG laser (λ = 1064 nm, Spectron Systems) is focused onto a rotating iron target to generate a hot metal plasma. Cluster formation occurs by synchronization of a helium pulse and subsequent supersonic expansion. After passing a skimmer, the ionic components of the molecular beam are transferred into the analyzer cell where they are trapped in the field of a 7.05 T superconducting magnet. The distribution of cluster ions thus produced can be somewhat controlled by varying the delays between helium pulse, laser shot, and subsequent inlet into the analyzer cell. Whereas the abundances achieved for Fe^+ and Fe_2^+ were quite high, those for the larger clusters were significantly lower, thereby complicating the experiments in such cases. After mass-selection of a specific cluster size and removal of peaks resulting from the ^{54}Fe and ^{57}Fe isotopes by means of the FERETS ion-ejection protocol,[33] the Fe_n^+ ions were thermalyzed by an argon pulse.

Ion-molecule reactions between Fe_n^+ and COS and CS_2, respectively, were then studied by leaking-in the neutral substrate at $p \approx 5 \cdot 10^{-9}$ to $2 \cdot 10^{-7}$ mbar and recording the decline of the reactant Fe_n^+ clusters and the evolution of the products. Bimolecular rate constants k (±30% uncertainty)[34] were derived on the basis of the pseudo-first-order approximation, and the corresponding reaction efficiencies $\varphi \equiv k/k_{cap}$ were calculated according to capture theory.[35] Consecutive reactions were analyzed using numerical routines.[36,37] For the reactivity studies of the $Fe_nS_x^+$ clusters, the reactant ions were prepared by pulsing-in COS to mass-selected Fe_n^+. After further mass selection, the reactions with the permanently leaked-in substrates were recorded similarly to the way described above.

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