Generation and Characterization of the Anionic, Neutral, and Cationic Iron–Dioxygen Adducts [FeO2] in the Gas Phase

Detlef Schröder,* Andreas Fiedler, Joseph Schwarz, and Helmut Schwarz*

Institut für Organische Chemie der Technischen Universität Berlin, Strasse des 17, Juni 135, D-10623 Berlin, Germany

Both the cations and anions of the elemental composition [FeO2] were generated by chemical ionization of a mixture of $Fe(CO)_5$ and O_2, and the connectivities of the ions were probed by various mass spectrometric methods. The neutral [FeO2] molecule was generated from either the anion and cation by means of neutralization reionization (NR) mass spectrometry. Collisional activation, charge reversal, and NR studies, as well as results of ion-molecule reactions of thermalized $[FeO_2]^+$ and $[FeO_2]^-$ ions with different substrates under the conditions of *Fourier transform* ion cyclotron resonance mass spectrometry, were employed to explore the potential energy hypersurfaces for both ions. The connectivities of the cations are best described as a *side-on* peroxo complex of the triplet dioxygen molecule with the metal cation, $Fe(O_2)^+$ (I), which easily isomerizes to the high-valent iron(V) dioxide, $OFeO^+$ (III). For the anion we suggest the structure of the iron(III) dioxide anion, $OFeO^-$. With respect to the neutral [FeO2] molecules, generated from the corresponding cation and anion by vertical electron transfer in the NR experiments, both connectivities seem to be stable on the mass spectrometric timescale. In addition, the energetics and binding situations in *side-on* and *end-on* $Fe(O_2)^+$ complexes as well as in the *inserted* iron dioxide cation, $OFeO^+$, were examined by means of *ab initio* MO calculations at the CASPT2D level of theory. The calculations predict a bond dissociation energy of 24 kcal/mol for the $^6A_1$ state of the C_{2v}-symmetrical *side-on* complex $Fe(O_2)^+$ (I) and of 29 kcal/mol for the $^6A_1$ state of bent $OFeO^+$ (III) with respect to isolated $Fe^+(^6D)$ and $O_2(^3\Sigma_g^-)$. These numbers agree well with the bracketed BDE of 25 ± 6 kcal. The interconversion of *side-on* $Fe(O_2)^+$ (I) to the energetically more stable $OFeO^+$ (III) and its implications for the interpretation of the mass spectrometric experiments are discussed.

Introduction

Transition metals in general, and iron in particular, play an essential role in the activation, transportation, and storage of molecular oxygen.[1] For the understanding of the basic principles of dioxygen activation, knowledge of the structures of dioxygen adducts with neutral or charged transition metal atoms and the reactivities of the corresponding complexes toward oxidizable organic substrates is a prerequisite. Recently, we demonstrated that cationic iron complexes exhibit a unique behavior as compared to the first row transition-metal congeners with regard to the simultaneous activation of molecular oxygen and of C–H and C–C bonds in the gas phase.[2] These results parallel the relevance of iron-containing complexes for the catalysis of oxidation processes in the condensed phase.

For the mononuclear [FeO2] molecule, first-principle considerations indicate that three basic structures are conceivable (Chart 1):[3,4] (i) a C_{2v}-symmetrical η^2-*side-on* complex of dioxygen with the iron atom (I), which may be looked at as either a peroxo complex or a metalladioxirane,[5] respectively; (ii) a linear or bent *end-on* η^1-coordination of dioxygen to the transition metal (II), which can also be described as a super-

Chart 1

I	II	III
η²-complex or peroxide	η¹-complex or superoxide	Iron dioxide
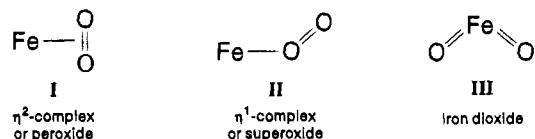
oxide; (iii) metal atom inserted in the O_2 molecule, resulting in a (linear or bent) high-valent iron dioxide (III).[6]

Previous spectroscopic studies on the structure(s) of the products formed when neutral iron atoms are reacted with molecular oxygen in rare-gas matrices established the existence of the neutral *side-on* complex I, which can be converted to the bent iron dioxide III upon irradiation with near-UV light.[7] Here, we report on the generation and structural characterization of anionic, neutral, and monocationic $[FeO_2]^{+/0/-}$ molecules in the gas phase by means of mass spectrometric techniques.[8] For the cationic system, the experimental results are complemented by high level *ab initio* MO calculations.

® Abstract published in *Advance ACS Abstracts*, September 15, 1994.

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## Experimental and Computational Details

Most of the experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors), which has been described previously.[9] Cationic and anionic ions $[FeO_2]^{+/-}$ were generated by bombarding a ca. 1:100 mixture of $Fe(CO)_5$ and O_2 with electrons having 100 eV kinetic energy in a chemical ionization source (repeller voltage ca. 0 V) in the positive or negative ion mode. Collisional activation (CA) was brought about by colliding a beam of $[FeO_2]^+$ cations, mass-selected using B(1)E(1) at a mass resolution of $m/\Delta m = 2500$, which was sufficient to resolve any isobaric interferences, with helium (85% transmission, T) in the field free region preceding B(2), and the resulting cationic fragments were recorded by scanning B(2). For neutralization—reionization (NR) experiments,[10,11] $[FeO_2]^+$ was mass-selected using B(1)E(1) at $m/\Delta m = 2500$ and subjected to a double collision experiment in the field-free region preceding B(2). Neutralization was performed by collision with xenon (80% T), the remaining ions were deflected by a 1000 V potential, the beam of fast neutrals subsequently reionized by collision with oxygen (80% T), and the so-formed cations were analyzed by scanning B(2). $[FeO_2]^-$ anions were mass-selected as described above and subjected to charge reversal (CR)[12] by collision with oxygen (70% T) in the field-free region preceding B(2). NRMS of $[FeO_2]^-$ to the corresponding cations ($^-NR^+$) was performed as described above for the cation, with the difference that molecular oxygen has been used in both collision events (80% T each). For collisional activation of $[FeO_2]^+$, produced by dissociative charge reversal of $[FeO_4]^-$ as described above,[13] the so-formed $[FeO_2]^+$ cations were mass-selected by means of B(2),

collisionally activated with helium (70% T) in the field-free region preceding E(2), and the ionic fragments were recorded by scanning E(2). All spectra were accumulated and on-line processed with the AMD/Intectra data system; 5—30 scans were averaged to improve the signal-to-noise-ratio. The reproducibility of the NR spectra amounts to ±10% for each ion signal intensity.

Additional experiments were performed with a Spectrospin CMS 47X Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, which has been described in detail elsewhere.[14] Fe^+ and $Fe(CO)^+$ were generated in the external ion source by laser desorption/laser ionization of an iron target and electron impact ionization of $Fe(CO)_5$, respectively. The cations were transferred by a system of electric potentials and lenses to the analyzer cell, which is located inside a superconducting magnet (maximum field strength 7.05 T). $Fe(CO)_n^-$ anions ($n = 0-4$) were generated by electron impact ionization of $Fe(CO)_5$ in the external ion source, using N_2O as electron moderating agent.[15] The ions of interest were isolated using the FERETS technique, a computer-controlled ion ejection protocol which combines single frequency ion ejection pulses with frequency sweeps to optimize ion isolation.[16] Rate constants and branching ratios were determined from the analysis of the pseudo-first-order kinetics.[8n] Reagent gases were introduced to the FTICR cell via either leak or pulsed valves. All data were accumulated and on-line processed using an ASPECT 3000 minicomputer. $^{18}O_2$ (>99% purity, 97—98 atom % ^{18}O) was purchased from CAMPRO Scientific, Emmerich, Germany.

Ab initio MO calculations on the cationic $[FeO_2]^+$ system were performed similar to the MO studies of the iron monoxide cation, which has been described in detail elsewhere.[17] Initially, geometry optimizations of the cations **I**, **II**, and **III** were performed using the approximate density functional theory[18] with the DGAUSS program (version 1.1.1)[19] employing the LCGTO-LSD approach (linear combination of Gaussian type orbitals, local spin density); this will be referred to as LSD. All stationary points were characterized as minima on the potential energy hypersurface by evaluating the vibrational frequencies and normal modes using analytical first derivatives and a finite difference scheme for the force-constant matrix. Subsequently, the low lying roots in all spatial and spin symmetries of the cations **I**, **II**, and **III** were optimized at the CASSCF as well as the CASPT2D[20] levels of theory using contracted Gaussian basis sets (9s5p1d)/[4s2p1d] for oxygen and a (14s10p6d1f)/[8s5p3d1f] basis set for the iron atom; this basis set will be referred to as BSI. The energies of the lowest lying quartet and sextet states for all structures were recalculated at the CASPT2D level using atomic natural orbital basis sets for oxygen (14s9p4d3f)/[4s3p2d] and an augmented basis set for iron (14s11p6d3f)/[8s7p4d1f]; this will be referred to as BSII. The geometry of the *inserted* structure **III** was reoptimized at this level of theory. In order to account for the remaining incompleteness of the basis sets, a further enlargement was made (BSIII): For the oxygen atom the basis set was less contracted as compared to BSII (14s9p4d3f)/[5s4p3d2f], and the basis set for the iron atom was further uncontracted and supplemented with one additional f and two g functions to (14s11p6d4f2g)/[8s7p4d4f2g].[21] The CAS calculations were performed using the MOLCAS-2 package.[22] The active MO space consists mostly of the 4s and 3d orbitals of the iron atom and the 2p orbitals of oxygen (15 electrons in 12 orbitals). All electrons were correlated at the CASPT2D level of theory. Bond

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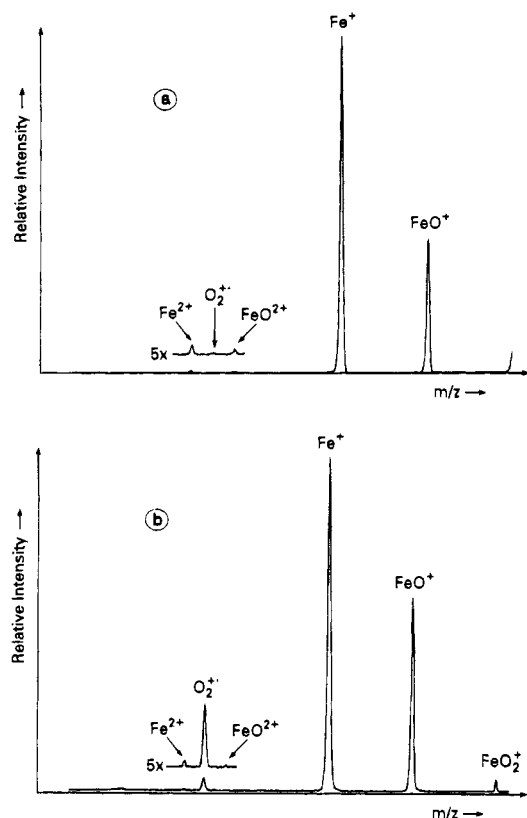
Figure 1. (a) CA mass spectrum of mass-selected $[FeO_2]^+$ (helium, 85% T). (b) NR mass spectrum of mass-selected $[FeO_2]^+$ (xenon/oxygen, each 80% T).

dissociation energies (BDEs) were derived from the sum of the energies of the isolated molecules. All computations were performed on either IBM/RS 6000 workstations or a CRAY-YMP computer.

Results and Discussion

If a ca. 1:100 mixture of $Fe(CO)_5$ and dioxygen is subjected to chemical ionization in the positive ion mode, $[FeO_2]^+$ is formed, most probably via the ligand exchange reaction $Fe(CO)^+ + O_2 \rightarrow [FeO_2]^+ + CO$. For an ion formed under the multiple collision conditions which prevail in a chemical ionization experiment, it is not entirely unexpected to observe that the $[FeO_2]^+$ ions do not undergo any significant unimolecular dissociation processes within the microsecond time scale.[23] Upon collisional activation, the Fe^+ and FeO^+ fragment ions dominate the CA spectrum; the signal for $O_2^{•+}$ is of negligible intensity (Figure 1a). In addition, very weak signals corresponding to the dications FeO^{2+} and Fe^{2+} are observed; these are formed presumably by charge stripping[24] of FeO^+ and Fe^+ or, alternatively, by rapid dissociation of doubly-charged $[FeO_2]^{2+}$. The signal for $[FeO_2]^{2+}$ hardly exceeds the signal to noise level, thus pointing to a low stability of this dication. Similarly, signals corresponding to Fe^+ and FeO^+ also dominate the NR mass spectrum of $[FeO_2]^+$ (Figure 1b). Note, that compared with the CA spectrum the signals for Fe^{2+} and FeO^{2+} dications are much less intense than that of $O_2^{•+}$. The observation of a signal corresponding to reionized neutral $[FeO_2]$ reveals that the neutral molecule is stable within the microsecond

time scale of the experiment, completely in line with previous matrix isolation studies.[7] The CA and NR mass spectra of mass-selected $[FeO_2]^+$ are in keeping with the description of this ion as the *side-on* (**I**) or *end-on* (**II**) ion—dipole complex of Fe^+ with molecular oxygen. This connectivity assignment is based on the following arguments: (i) The signal corresponding to $O_2^{•+}$ in the NR-spectrum indicates that the O—O-bond in $[FeO_2]^+$ is still intact. Upon vertical neutralization of $[FeO_2]^+$, an unknown proportion of the neutrals will fall apart to Fe and O_2; these fast moving neutrals are subsequently reionized to Fe^+ and $O_2^{•+}$. (ii) In both the CA and the NR spectra the signal corresponding to Fe^+ is more intense than that of FeO^+. Irrespective of the products' thermochemistry, for the *inserted* species **III** simple RRKM arguments predict that O atom loss is expected to favor formation of FeO^+ as compared to Fe^+ in a high energy collision event. However, the relatively high amount of the FeO^+ fragment is not entirely expected for the simple ligand complexes **I** and **II**. Thus, we cannot rule out the presence of structure **III**. We will return to this aspect in connection with the *ab initio* MO calculations further below. Although we cannot distinguish between structures **I** and **II** by means of mass spectrometric experiments, earlier theoretical considerations predicted the *side-on* coordination **I** as the energetically most stable cationic isomer;[6] this was also concluded from matrix studies for the neutral complex.[7]
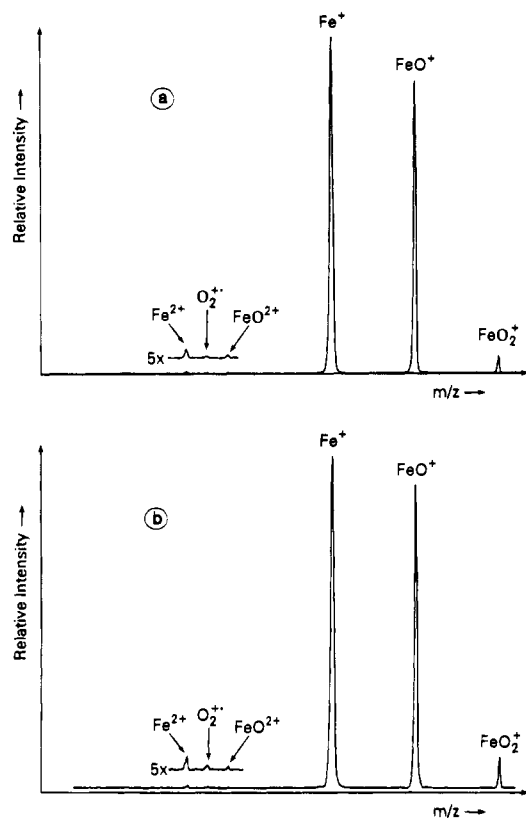
Upon negative chemical ionization of $Fe(CO)_5$ in the presence of O_2 the $[FeO_n]^-$ anions ($n = 2, 3, 4$) are formed, presumably in consecutive oxidation reactions of the type $Fe(CO)_n^- + O_2 \rightarrow Fe(CO)_mO_n^- (m + n \le 4) + CO_2$, which are known to occur under CI conditions.[25] The CR- and NR-spectra of $[FeO_2]^-$ are very similar to each other (Figure 2a,b), and the signal corresponding to reionized $[FeO_2]$ further substantiate the stability of the neutral molecule. As found for the cationic species, signals corresponding to Fe^+ and FeO^+ dominate the spectra, but their ratio changes significantly from 5:3 in the case of $[FeO_2]^+$ to almost 1:1 in the NR spectrum of $[FeO_2]^-$. Furthermore, hardly any $O_2^{•+}$ signal is observed either in the CR- or in the NR spectrum of the anion. These observations point to the formation of the inserted iron dioxide structure $OFeO^-$ (**III**) in the case of the anion, in which iron formally attains its well-known Fe(III) oxidation state. For the sake of completeness, we briefly mention the $^-NR^+$ data for $[FeO_3]^-$ and $[FeO_4]^-$ anions, respectively (relative intensities in % base peak, CR data are given in parentheses: for $[FeO_3]^-$, FeO_3^+ 4 (2), FeO_2^+ 6 (8), FeO^+ 100 (75), Fe^+ 95 (100), FeO^{2+} < 1 (1), $O_2^{•+}$ (<1), Fe^{2+} 1 (2), $O^{•+}$ 1 (<1); for $[FeO_4]^-$, FeO_4^+ 4 (2), FeO_3^+ <1 (<1), FeO_2^+ 10 (15), FeO^+ 65 (45), Fe^+ 100 (100), FeO^{2+} <1 (1), $O_2^{•+}$ 5 (1), Fe^{2+} 1 (2), $O^{•+}$ 1 (<1). On the basis of previous arguments, with respect to the $O_2^{•+}$ signal intensities, the data indicate an iron(V) trioxide structure for $[FeO_3]^-$, but at least one intact O—O unit in $[FeO_4]^-$.

In order to elucidate whether upon charge reversal the connectivity of the anion $[FeO_2]^-$ remains unchanged or whether in the course of the multicollision events rearrangement will take place, $[FeO_2]^+$ was generated independently by dissociative charge reversal of $[FeO_4]^-$ followed by a subsequent collisional activation experiment to probe the connectivity.[13] Within experimental error the spectrum of the so-formed cation is identical with that of authentic $[FeO_2]^+$ generated in the positive chemical ionization mode.[26] Thus, under CR conditions the cationic molecule can undergo the rearrangement **III** → **I** as will be discussed further below. However, the rearrangement

(23) $[FeO_2]^+$ decomposes unimolecularly to Fe^+ (100%) and FeO^+ (35%); however, the total abundance of these ions is less than 0.01% relative to the non-decomposing parent ion $[FeO_2]^+$, and the similarity to the CA-spectrum (Figure 1a) indicates that collision induced fragmentation of $[FeO_2]^+$ by residual gas within the field-free region is likely to contribute to the metastable ion spectrum.
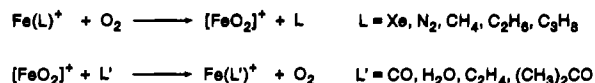
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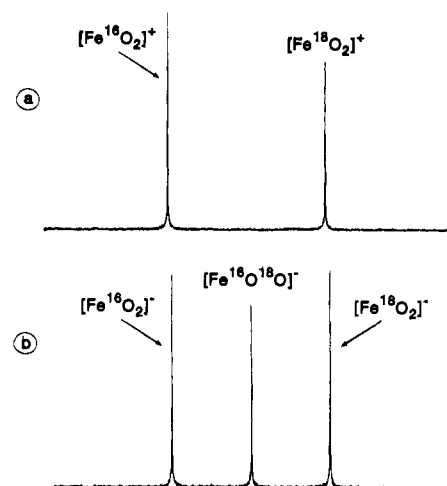
Figure 3. Thermoneutral isotopic exchange reactions of mass selected [$Fe^{18}O_2$]$^{+/-}$ ions with $^{16}O_2$ under FTICR conditions: (a) ion—molecule reaction of [$Fe^{18}O_2$]$^+$ with $^{16}O_2$; (b) ion—molecule reaction of [$Fe^{18}O_2$]$^-$ with $^{16}O_2$.

Scheme 2

$$Fe(L)^+ + O_2 \longrightarrow [FeO_2]^+ + L \qquad L = Xe, N_2, CH_4, C_2H_6, C_3H_8$$

$$[FeO_2]^+ + L' \longrightarrow Fe(L')^+ + O_2 \qquad L' = CO, H_2O, C_2H_4, (CH_3)_2CO$$

Figure 2. (a) CR mass spectrum of mass-selected [FeO_2]$^-$ (oxygen, 70% *T*). (b) $^-NR^+$ mass spectrum of mass-selected [FeO_2]$^-$ (oxygen/oxygen, each 80% *T*).

Scheme 1

$$Fe(L)^+ + O_2 \longrightarrow [FeO_2]^+ + L \qquad L = Xe, N_2, CH_4, C_2H_6, C_3H_8$$

$$[FeO_2]^+ + L' \longrightarrow Fe(L')^+ + O_2 \qquad L' = CO, H_2O, C_2H_4, (CH_3)_2CO$$

III → I does not seem to take place for neutral **III** as indicated by the similarity of the CR and NR spectra (Figure 2a,b). Thus, the elusive neutral iron(IV) dioxide is a viable molecule in the gas phase.[27]

In order to further substantiate the structural assignments for the cationic and the anionic species, we examined ion—molecule reactions of thermalized [FeO_2]$^{+/-}$ ions under FTICR conditions. [FeO_2]$^+$ was formed by exothermic ligand exchange reactions of dioxygen with thermalized Fe(L)$^+$ complexes, with L = Xe, N$_2$, CH$_4$, C$_2$H$_6$, and C$_3$H$_8$, respectively (Scheme 1).[28] The occurrence of these displacement reactions allows the determination of a lower limit for BDE(Fe$^+$—O$_2$), which exceeds BDE-(Fe$^+$—C$_3$H$_8$) = 19 kcal/mol.[30] An upper limit of BDE (Fe$^+$—O$_2$) < 32 kcal/mol is obtained by the observation that displacement of the dioxygen ligand in thermalized [FeO_2]$^+$

takes place with more strongly bonded ligands L' (L' = CO, H$_2$O, C$_2$H$_4$, and (CH$_3$)$_2$CO).[31] These ligand exchange reactions are in line with the presence of an intact dioxygen entity and support the assignment of structure **I** for the cationic species. However, since no accurately determined ligand binding energies in this energy regime are known for Fe$^+$, we are unable to narrow the lower and upper limits for BDE(Fe$^+$—O$_2$).[35]

For yet another test of the ion structure, [$Fe^{18}O_2$]$^+$ was generated by reacting nonthermalized[36,37] Fe(CO)$^+$ with an excess of pulsed-in $^{18}O_2$, subsequently isolated, collisionally cooled, and reacted with $^{16}O_2$ (Scheme 2, Figure 3). In this thermoneutral reaction a rapid exchange of the dioxygen molecule occurs to yield [$Fe^{16}O_2$]$^+$.[38] Consecutive $^{16}O/^{18}O$ isotopic scrambling is not observed; i.e., [$Fe^{16}O^{18}O$]$^+$ is not formed at all. Both findings are, again, in line with structure **I** and disfavor the dioxide structure **III** for the cation (*vide infra*). In contrast, in the ion—molecule reaction of isolated [$Fe^{18}O_2$]$^-$ anions with $^{16}O_2$, the oxygen atoms exchange consecutively,[38]

(26) In view of their similarity the MS^3 spectra are not reproduced as figures. The corresponding CA data are as follows: [FeO$_2$]$^+$ from CR of [FeO$_4$]$^-$, FeO$^+$ 35%, Fe$^+$ 100%; [FeO$_2$]$^+$ from Fe(CO)$_5$/O$_2$ in the positive CI mode, FeO$^+$ 30%, Fe$^+$ 100%.

(27) There is also some speculation in the literature for the existence of neutral [FeO$_2$] in the condensed phase; however, this substance is not very well characterized: Addison, C. C.; Logan, B. F. G.; Logan, N. *J. Chem. Soc.* **1965**, 4490.

(28) Fe(L)$^+$ ions were generated by ligand exchange reactions of Fe(CO$_2$)$^+$ with the corresponding neutral L.[29] Fe(C$_2$H$_6$)$^+$ was also formed by reacting bare Fe$^+$ with acetone.[30]

(29) Fe(CO$_2$)$^+$ is formed in good yield in the reaction of thermalized Fe$^+$ with β-butyrolactone: Schwarz, J.; Schwarz, H. *Organometallics* **1994**, *13*, 1518.

(30) (a) Schultz, R. H.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 729. (b) Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1992**, *96*, 1662.

(31) BDE(Fe$^+$—CO) = 32 kcal/mol;[32] BDE(Fe$^+$—OH$_2$) = 32 kcal/mol;[33] BDE(Fe$^+$—C$_2$H$_4$) = 34 kcal/mol;[34] BDE(Fe$^+$—acetone) = 40 kcal/mol.[8n]

(32) The BDE of Fe(CO)$^+$ is a matter of controversy; the most recent value amounts to ca. 32 kcal/mol (Dalleska, N. F.; Armentrout, P. B. University of Utah, private communication). For a detailed discussion of BDE(Fe$^+$—CO) and leading references, see: Schultz, R. H.; Crellin, K. C.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 8590.

(33) (a) Magnera, T. F.; David, D. E.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 4100. (b) Fiedler, A.; Hrušák, J.; Schwarz, H. *Z. Phys. Chem.* **1992**, *175*, 15. (c) Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1993**, *97*, 596.

(34) Freiser, B. S. *Chemtracts-Anal. Phys. Chem.* **1989**, *65*, 1.

(35) Additional thermochemical data were taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(36) Due to the injection of the Fe(CO)$^+$ ions from the external ion source into the FTICR cell, prior to thermalization these ions possess excess kinetic energy which, however, cannot exceed the trapping potentials of 1.0 V. In the center-of-mass energy frame this then limits the excess energy to ≤6 kcal/mol, which favor the rapid ligand exchange of Fe-(CO)$^+$ with dioxygen. In addition, the ions formed by electron impact ionization of Fe(CO)$_5$ may also be electronically excited.

(37) If thermalized Fe(CO)$^+$ is reacted with O$_2$, oxidation to FeO$^+$ and CO$_2$ takes place and efficiently competes with ligand exchange to yield Fe(O$_2$)$^+$.

Table 1. Optimized Geometries of the [FeO₂]⁺ Compounds **I**, **II**, and **III** Using the LSD Approach[a,b]

structure	multiplicity	r_{Fe-O}	r_{O-O}[c]	α[d]
side-on (**I**)	quartet	1.71	1.37	
	sextet	1.84	1.35	
end-on (**II**)	quartet	1.71	1.25	140
	sextet	1.77	1.24	140
inserted (**III**)	quartet	1.56	2.61	114
	sextet	1.63	2.23	86

[a] Bond lengths in Å and angles in deg. [b] Linear *end-on* structures were characterized as transition structures at the LSD level of theory. [c] The experimental value of isolated dioxygen amounts to $r_{O-O} = 1.22$ Å; this bond length is perfectly reproduced using the LSD approach. [d] The angles α refer to α(FeOO) for the *end-on* and α(OFeO) for the *inserted* structure (Chart 2).

Chart 2. Optimized Geometries of Cationic **I**, **II**, and **III** Using the LSD Approach, with Bond Lengths in Å, Bond Angles in deg, and the Charges Given Being Derived from a Mulliken Population Analysis

I   **II**

III
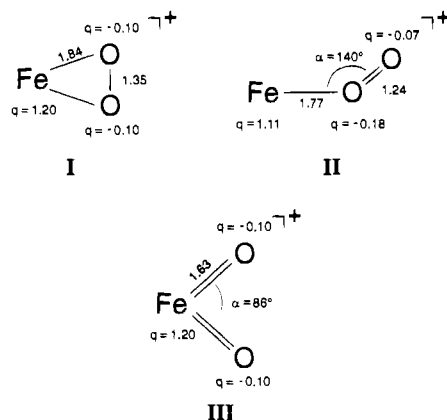
to yield both [Fe¹⁶O¹⁸O]⁻ as well as [Fe¹⁶O₂]⁻. This result is precisely expected for an iron(III) dioxide structure, **III**.

However, in a strict sense the assignment of ion structures from CA or NR spectra of a single isomer is not necessarily unambiguous. In particular, as mentioned above the structural assignment for [FeO₂]⁺ corresponding to **I** rather than **III** is not absolutely conclusive. Therefore, we performed several experiments aimed at generating [FeO₂]⁺ by entirely different routes. However, all attempts to generate *cationic* **III** via an independent path failed or led to the same CA spectra as that displayed in Figure 1a, e.g. reaction of FeO⁺ with O-atom donors like oxirane, nitrogen dioxide, and ozone or electron impact ionization of anhydrous iron(III) nitrate.

In order to gain further information on the structures of *cationic* [FeO₂]⁺ species we performed *ab initio* MO calculations at the LSD and CASPT2D levels of theory for the *side-on* (**I**) and *end-on* (**II**) iron—dioxygen complexes as well as the *inserted* dioxide (**III**). First, the geometries of the sextet and quartet states of **I**—**III** were optimized using the LSD method (Table 1). According to the Mulliken population analysis of the C_{2v}-symmetrical sextet *side-on* complex **I**, the positive charge q on the iron atom increases upon the approach of the electronegative dioxygen ligand (Chart 2). Actually, the binding situation in **I** suggests that this species is best described in terms of a peroxo complex or a metalladioxirane.[5] The O—O bond

Table 2. Harmonic Vibrational Frequencies (cm⁻¹) for the [FeO₂]⁺ Compounds **I**, **II**, and **III** Using the LSD Approach

structure	multiplicity	ν_1	ν_2	ν_3
side-on (**I**)	quartet	1234	1178	627
	sextet	1084	489	453
end-on (**II**)	quartet	1459	546	153
	sextet	1425	559	229
inserted (**III**)	quartet	1032	987	316
	sextet	931	750	271

Table 3. Total Energies (hartrees) of All Possible Symmetries of [FeO₂]⁺ on the CASSCF/BSI//LSD and CASPT2D/BSI//LSD Levels of Theory[a]

structure	state	CASSCF	CASPT2D
side-on (**I**)	⁴B₁	−1411.80988	−1412.61361
	⁴A₂	−1411.80109	−1412.59753
	⁴B₂	−1411.76992	−1412.57011
	⁴A₁	−1411.76576	−1412.55053
	⁶A₁	−1411.83924	−1412.63130
	⁶A₂	−1411.83437	−1412.61988
	⁶B₁	−1411.77131	−1412.54472
	⁶B₂	−1411.76195	−1412.53219
end-on (**II**)	⁴A″	−1411.81756	−1412.59032
	⁴A′	−1411.81362	−1412.58974
	⁶A″	−1411.82192	−1412.58274
	⁶A′	−1411.78381	−1412.54844
inserted (**III**)	⁴B₂	−1411.79275	−1412.63466
	⁴B₁	−1411.79474	−1412.63254
	⁴A₂	−1411.75390	−1412.59342
	⁴A₁	−1411.73554	−1412.58440
	⁶A₁	−1411.78888	−1412.63608
	⁶B₂	−1411.73073	−1412.58487
	⁶B₁	−1411.71803	−1412.56520
	⁶A₂	−1411.71364	−1412.55395

[a] The lowest-lying ²B₂ doublet state of **III** is more than 3 eV higher in energy than **III** (⁶A₁).

length increases significantly to $r_{O-O} = 1.35$ Å as compared to $r_{O-O} = 1.22$ Å in the isolated dioxygen molecule and corresponds to the bond length in $O_2^{\bullet-}$ (r_{O-O}-(exptl) = 1.35 Å)[4d]; the Fe—O distance ($r_{Fe-O} = 1.84$ Å) is comparable[17] to that of covalent Fe—O bonds in cationic systems.[39] In contrast, in the quartet and the sextet states of the *end-on* complex **II**, the O—O bond length remains almost unperturbed as compared to isolated dioxygen. The inserted species **III** can indeed be described as a formally high-valent iron(V) compound, since r_{Fe-O} is comparable[17] to that of the formal iron(III) compound FeO⁺, and the large O—O distance prevents a noticeable bonding interaction between the oxygen atoms as in **I** and **II**. Although the geometry of the *inserted* species **III** largely differs from those of **I** and **II**, it is strongly bent, α(OFeO) = 86°, indicating the possibility of the interconversion **I** ⇌ **III** along the a₁ vibrational mode. The vibrational frequencies (Table 2) demonstrate that **I**, **II**, and **III** correspond to minima on the potential energy hypersurface, and their magnitudes are in line with the structural assignments.

Next, the total energies of all possible symmetries of the quartet and the sextet spin states of **I**, **II**, and **III** were calculated at the CASSCF as well as the CASPT2D levels of theories using BSI (Table 3). At the CASPT2D/BSI//LSD level of theory the energetically lowest lying electronic state of the dioxygen complexes corresponds to the *side-on* complex **I** with ⁶A₁ symmetry. The lowest-lying quartet electromer (⁴B₁) of **I** is ca. 0.5 eV higher in energy than the ⁶A₁ state. The quartet and sextet states of the *end-on* complex **II** are much less stable than the ⁶A₁ *side-on* complex **I**. Surprisingly, the ⁶A₁ state of the

(38) The absolute rate constants (±25%[8n]) for the ion—molecule reactions described in Scheme 2 are 2.7 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for the reaction of Fe(¹⁸O₂)⁺ with ¹⁶O₂, and 2.4 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for the reaction of Fe(¹⁸O₂)⁻ with ¹⁶O₂, respectively. These rates are approximately half of the maximum collision rate constants (6.1 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for both reactions), as expected for a thermoneutral isotope exchange reaction.

(39) (a) Schröder, D.; Fiedler, A.; Hrušák, J.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 1215. (b) Fiedler, A. Diploma Thesis, TU Berlin, 1992. (c) Reference 17.
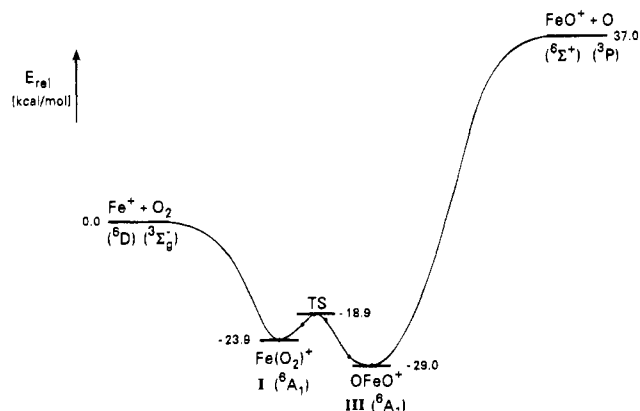
Table 4. Total Energies (hartrees) of Low-Lying States of $[FeO_2]^+$ on the CASSCF/BSII//LSD and CASPT2D/BSII//LSD Levels of Theory

structure	state	CASSCF	CASPT2D
side-on (**I**)	$^4B_1$	−1411.84527	−1412.83733
	$^6A_1$	−1411.87771	−1412.85369
	$^6A_2$	−1411.87297	−1412.84246
end-on (**II**)	$^4A''$	−1411.84811	−1412.80803
	$^6A''$	−1411.85185	−1412.79845
inserted (**III**)	$^4B_2$	−1411.83198	−1412.86035
	$^4B_1$	−1411.83350	−1412.85733
	$^6A_1$	−1411.82609	−1412.86181
Fe^+	^6D	−1262.13451	−1262.73045
O_2	$^3\Sigma_g^-$	−149.75894	−150.08514

inserted structure **III** is 3.0 kcal/mol lower in energy than **I** ($^6A_1$), although $OFeO^+$ corresponds formally to a high-valent Fe(V) compound. We note in passing that the comparison of the CASSCF and CASPT2D results reveals the importance of dynamic correlation for an appropriate description of metal−ligand features as compared with the bonding of molecules containing first- and second-row elements.[17]

In order to further refine the energetics of the low-lying states of $[FeO_2]^+$, these were calculated using the extended basis set BSII (Table 4). The binding energy of the $^6A_1$ *side-on* complex with respect to the dissociation into Fe^+ (^6D) and O_2 ($^3\Sigma_g^-$) increases from 16.8 kcal/mol with BSI to 23.9 kcal/mol using BSII. Similarly, the BDE of **III** increases from 19.8 to 29.0 kcal/mol. We note that the extension of the basis set does not alter the sequence of relative stabilities of the quartet and sextet states for **I**, **II**, and **III**. In order to test, if the LSD optimized geometries are consistent with the results obtained with CASPT2D, the structure of the energetically most stable $^6A_1$ electrometer of the *inserted* structure **III** was reoptimized at the CASPT2D/BSII level of theory. As expected from previous studies,[40] geometry optimization of **III** leads to an increase of r_{Fe-O} to 1.70 Å, whereas $\alpha(OFeO)$ and r_{O-O} remain almost unperturbed (84.3° and 2.28 Å, respectively). These geometry changes result in a increase of the binding energy by 1.6 kcal/mol; however, this minor effect demonstrates that already the LSD procedure yields a reliable description of the geometry. Finally, the effect of a further enlargement of the basis set was evaluated by inclusion of higher angular momentum functions (BSIII), resulting in an increase of the binding energy by further 2.6 kcal/mol. Both the minor effects of the geometry reoptimization and the use of a very large basis set indicate that the energetics of the $[FeO_2]^+$ system is quite reliably described by this theoretical approach. On the CASPT2D/BSIII//CASPT2D/BSII level of theory the stabilization energy of the $^6A_1$ state of **III** amounts to 33.2 kcal/mol with respect to isolated Fe^+ (^6D) and O_2 ($^3\Sigma_g^-$).

According to the theoretical results the iron dioxide **III** corresponds to the global minimum of the $[FeO_2]^+$ hypersurface. In view of this finding, we felt obliged to reconsider the structural assignment for $[FeO_2]^+$ based on the mass-spectrometric experiments discussed above. In particular, if the interconversion **I** ⇌ **III** is energetically feasible, the experiments will not be conclusive. More precisely, if the energy demand of the transition structure (TS) connecting **I** and **III** is significantly lower than the Fe^+-O_2 binding energy, both structures will be populated and may contribute to the observed reactivity. For example, the exclusive exchange of the intact $^{18}O_2$ unit in $[Fe^{18}O_2]^+$ by $^{16}O_2$ can be rationalized by the mechanism as depicted in Scheme 3. Consecutive $^{18}O/^{16}O$ atom

(40) (a) Fan, L.; Ziegler, T. *J. Chem. Phys.* **1991**, *95*, 7401. (b) Ziegler, T.; Li, J. *Can. J. Chem.*, submitted for publication.

Figure 4. Potential energy hypersurface (kcal/mol) for $[FeO_2]^+$ ($^6A_1$) at the CASPT2D/BSII//LSD level of theory. The dots between structures **I** and **III** represent the result of the linear synchronous transit; see text for details.

Scheme 3
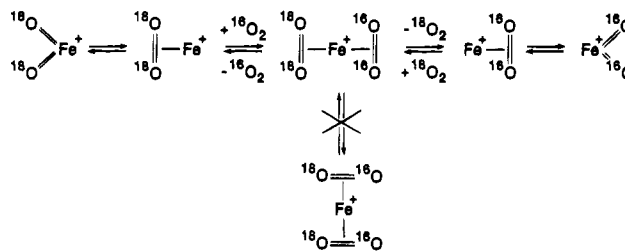
exchange, which is not observed experimentally (Figure 3) would only occur, if Fe^+ is able to activate the O−O bonds of the two dioxygen ligands simultaneously.

Consequently, we examined the interconversion **I** ⇌ **III** by theoretical means. To begin with, this process is considered to be symmetry-allowed since spin multiplicity and symmetry are conserved; i.e., **I** ($^6A_1$) → **III** ($^6A_1$). Due to the lack of analytical gradients, the CASPT2D procedure applied here does not allow a transition state search with reasonable expenditure. Therefore, two alternative approaches were used to tackle this problem: (i) The first is a linear synchronous transit (LST)[41] between **I** and **III** at the CASPT2D/BSII level of theory. Here, the geometry differences Δr_i of the intermediate structures en route from **I** to **III** are mimicked by variation of a linear factor σ between 0 and 1 for both Δr_{Fe-O} and Δr_{O-O}.[42] (ii) The CASPT2D/BSII energy of the TS, as located by using the LSD approach, was evaluated by a single point calculation.[43] Figure 4 displays the energetics of the $[FeO_2]^+$ system by using the LST procedure. Interestingly, the energy needed for the interconversion **I** ⇌ **III** is quite low (5.0 kcal/mol), and the transition state is by 18.9 kcal/mol *lower* than the energy demand for the dissociation into Fe^+ and O_2; thus, the interconversion **I** ⇌ **III** is likely to occur. This finding agrees well with the calculated energy of the TS located on the LSD level of theory (18.4 kcal/mol with respect to dissociation). Furthermore, the magnitude of the imaginary frequency of the TS ($732i$ cm^{-1}) is

(41) (a) Hänsele, E.; Clark, T. *Z. Phys. Chem.* **1991**, *171*, 21. See also: (b) Hada, M.; Nakatsuji, H.; Nakai, H.; Gyobu, S.; Miki, S. *J. Mol. Struct. (THEOCHEM)* **1993**, *281*, 207.

(42) Energies E(σ) of the LST structures relative to Fe^+ and O_2 for various values of σ (Figure 4): E(0.0) = E(**I**) = 23.9 kcal/mol; E(0.25) = 20.8 kcal/mol; E(0.375) = 18.9 kcal/mol; E(0.5) = 19.9 kcal/mol; E(0.75) = 27.3 kcal/mol; E(1.0) = E(**III**) = 29.0 kcal/mol. For σ = 0.375 the geometry corresponds to r_{Fe-O} = 1.77 Å, r_{O-O} = 1.69 Å, and α = 57.1°.

(43) Geometry of the LSD-optimized TS: r_{Fe-O} = 1.69 Å, r_{O-O} = 1.71 Å, and α = 60.9°. Frequencies: v_1 = 917 cm^{-1}, v_2 = 709 cm^{-1}, and v_i = $732i$ cm^{-1}.

in line with a synchronous motion of all atoms and a relatively flat hypersurface between **I** and **III**. In view of experimental and theoretical errors, the energetics as displayed in Figure 4 are well compatible with the lower and upper bounds as derived from the ion-molecule reactions described above.

The facile interconversion of cation **I** $\rightleftharpoons$ **III** sheds new light on the mass spectrometric experiments to the extent that both isomers will contribute to the observed reactivity and fragmentation patterns. For example, the ligand exchange reactions as well as the $O_2^{\bullet+}$ signal in the NR spectrum of $[FeO_2]^+$ can be associated to structure **I**, whereas the FeO^+ fragment originates from **III**. The ambivalent character of the $[FeO_2]^+$ system is further exemplified by its ion—molecule reaction with benzene, in which ligand displacement to yield $Fe(C_6H_6)^+$ and O_2 competes with charge exchange to yield $C_6H_6^{\bullet+}$ and neutral FeO_2 (Scheme 4): Here, the exchange of dioxygen by the stronger bound benzene ligand[44] can be attributed to structure **I**. The observation of charge exchange implies that the ionization energies (IE) of the neutral $[FeO_2]$ formed in this process exceeds that of benzene (IE = 9.2 eV);[35] this is in line with the previously reported IE (FeO_2) of 9.5 eV,[8b] which is associated with the formation of neutral **III**. In contrast, according to our results and most recent *ab initio* calculations of the neutral species,[45] the IE of **I** does not exceed 8.7 eV; thus, exothermic charge exchange with benzene is impossible for the ground-state structure **I**. Hence, the mass spectrometric experiments do not permit an unambiguous distinction between **I** and **III**; a similar situation of interconverting isomers has recently been encountered for $Fe(C_2H_6)^+$ and $Fe(CH_3)_2^+$.[30b]

Conclusions

Chemical ionization of a mixture of $Fe(CO)_5$ and O_2 in either the positive or the negative mode affords $[FeO_2]^{+/-}$ ions, i.e. the cationic and anionic iron dioxides $OFeO^{+/-}$. *Ab initio* MO computations as well as the mass spectrometric studies indicate that the formal iron(V) compound $OFeO^+$ (**III**) can easily interconvert into the *side-on* dioxygen complex $Fe(O_2)^+$ (**I**); thus, both isomers are in equilibrium with each other. For the

Scheme 4
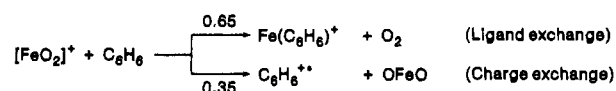
anion as well as the cation recovery signals are observed in a NR experiment corresponding to reionized $[FeO_2]$, and in view of the vertical nature[46] of these electron transfer processes it is likely that the connectivities of **I** and **III** are preserved in the formation of the neutral $[FeO_2]$ species. These findings are in line with the results of previous spectroscopic studies of the interaction of neutral Fe atoms with dioxygen in O_2-doped rare-gas matrices, in which it was demonstrated that the neutral *side-on* complex **I** gives rise to a stable neutral, from which neutral **III** can be formed by photochemical isomerization of **I**, whereas no evidence for an *end-on* structure **II** was found.[7]

From a chemical point of view, the facile interconversion of $Fe(O_2)^+$ into the high valent iron(V) compound $OFeO^+$ can serve as a rationalization for the previously reported[2] Fe^+-mediated simultaneous activation of olefins and dioxygen in the gas phase. In addition, the findings represent a simple model for the high activity of iron with respect to the activation of molecular oxygen in the condensed phase. In future work, we will examine the effect of additional ligands on charged as well as neutral metal atoms on the coordination of dioxygen[47] as well as its effects on the equilibrium between **I** and **III**. Furthermore, we will study the reactivity of these ions with respect to oxygen atom transfer to organic substrates.

(44) BDE (Fe^+-C_6H_6) = 55 kcal/mol (Ref. 34).

(45) Helmer, M.; Plane, J. M. C. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 395.

(46) (a) Fournier, P.; Appell, J.; Fehsenfeld, F. C.; Durup, J. *J. Phys. B* **1972**, *5*, L58. (b) Lorquet, J. C.; Ley-Nihaut, B.; McLafferty, F. W. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 465.

(47) For recent findings on dioxygen complexes and further references, see: (a) Reference 4b. (b) Kirchner, K.; Mauthner, K.; Mereiter, K.; Schmid, R. *J. Chem. Soc. Chem. Commun.* **1993**, 892. (c) Kahlow, M. A.; Loehr, T. M.; Zuberi, T. M.; Gennis, R. B. *J. Am. Chem. Soc.* **1993**, *115*, 5845.