Dissociation Patterns of Small $\mathrm{Fe}_m\mathrm{O}_n^+$ ($m = 1–4$, $n \leq 6$) Cluster Cations Formed Upon Chemical Ionization of $\mathrm{Fe(CO)_5/O_2}$ Mixtures

Detlef Schröder,[a] Phillip Jackson,[a] and Helmut Schwarz*[a]

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The collisional activation mass spectra of cationic iron oxide clusters $\mathrm{Fe}_m\mathrm{O}_n^+$ ($m = 1–4$, $n \leq 6$) prepared by chemical ionization of $\mathrm{Fe(CO)_5/O_2}$ mixtures show remarkable trends in the fragmentation behaviors, which can be attributed to the formal oxidation states of iron. (i) The preferential fragmentation pathways of $\mathrm{Fe}_m\mathrm{O}_n^+$ clusters with $m/n \geq 1$ correspond to losses of atomic oxygen as well as FeO units. (ii) For $\mathrm{Fe}_m\mathrm{O}_n^+$ clusters with $1 > m/n > 2/3$, losses of neutral $\mathrm{FeO_2}$ begin to compete with those of O and FeO. (iii) For $\mathrm{FeO_2^+}$ and the oxygen-rich clusters $\mathrm{Fe_2O_3^+}$ and $\mathrm{Fe_4O_6^+}$ ($m/n = 2/3$), losses of molecular oxygen predominate, while this channel is more or less irrelevant for the other $\mathrm{Fe}_m\mathrm{O}_n^+$ cations. These observations are interpreted using peroxide structures for the oxygen-rich $\mathrm{Fe}_m\mathrm{O}_n^+$ ions, thereby preventing the need for formal high-valent iron(IV) in these clusters.

Introduction

Ionic iron oxide clusters $\mathrm{Fe}m\mathrm{O}_n^{+/-}$ can be generated by sputtering neutral iron oxide,[1,2] by seeding Smalley-type expansion sources for iron clusters with oxygen,[3–5] or by reacting cationic Fe_m^+ clusters with suitable oxidants.[6–10] As far as cations are concerned, most of these methods are restricted to metal-rich clusters with $m/n \geq 1$, i.e. clusters containing iron in formal oxidation states up to $\mathrm{Fe^{III}}$. High-valent metal-oxo species that are potentially attractive as oxidants (e.g. the dinuclear $\mathrm{Fe^{IV}}$ oxide core of methane monooxygenase)[11,12] are usually not formed.

A viable approach for synthesizing oxygen-rich Fe/O clusters in the gas phase is by means of redox reactions, which we refer to hereafter as the chemical route to metal-oxide clusters.[6,13] Upon chemical ionization of a mixture of $\mathrm{Fe(CO)_5}$ with an excess of oxygen, a complex sequence of reactions occurs that ultimately leads to the formation of oxygen-rich $\mathrm{Fe}_m\mathrm{O}_n^+$ clusters [see Equations (1) – (5)].

Ionization

$$\mathrm{O_2 + e \rightarrow O_2^+ + 2e} \tag{1}$$

Charge transfer

$$\mathrm{Fe(CO)_5 + O_2^+ \rightarrow Fe(CO)}_n^+ + n\mathrm{CO + O_2} \tag{2}$$

Clustering

$$\mathrm{Fe(CO)}_n^+ + \mathrm{Fe(CO)_5} \rightarrow \mathrm{Fe_2(CO)}_m^+ + (5 + n - m)\mathrm{CO} \tag{3}$$

Oxidation

$$\mathrm{Fe_2(CO)}_m^+ + \mathrm{O_2} \rightarrow \mathrm{Fe_2O(CO)}_p^+ + \mathrm{CO_2} + (m - p - 1)\mathrm{CO} \tag{4}$$

$$\mathrm{Fe_2O(CO)}_p^+ + \mathrm{O_2} \rightarrow \mathrm{Fe_2O_2^+} + \mathrm{CO_2} + (p - 1)\mathrm{CO} \tag{5}$$

Let us illustrate this manifold by describing a plausible route for the formation of $\mathrm{Fe_2O_2^+}$ as an example. The sequence starts with electron ionization of $\mathrm{O_2}$ as the major component of the neutral mixture [Equation (1)], followed by (dissociative) charge transfer to yield iron-carbonyl cations [Equation (2)]. These ions then undergo clustering with neutral $\mathrm{Fe(CO)_5}$ to afford dinuclear iron-carbonyl clusters [Equation (3)],[6,14,15] followed by stepwise oxidation of the clusters by dioxygen [Equations (4) and (5)].[6,16] Side reactions lead to $\mathrm{Fe_2O_3^+}$ and trace amounts of $\mathrm{Fe_2O^+}$ (see below). Similarly, higher $\mathrm{Fe}_m\mathrm{O}_n^+$ clusters are accessible through this scheme, and their abundances very much depend on the $\mathrm{Fe(CO)_5/O_2}$ mixing ratios and other ionization parameters such as overall pressure, repeller voltage etc. Under typical CI conditions, reasonably intense signals can be achieved for (i) $\mathrm{FeO^+}$ and $\mathrm{FeO_2^+}$, (ii) $\mathrm{Fe_2O_2^+}$ and $\mathrm{Fe_2O_3^+}$, (iii) $\mathrm{Fe_3O_3^+}$ and $\mathrm{Fe_3O_4^+}$, as well as (iv) $\mathrm{Fe_4O_4^+}$, $\mathrm{Fe_4O_5^+}$, and $\mathrm{Fe_4O_6^+}$ (Table 1). More abundant $\mathrm{Fe_2O^+}$ fluxes than those obtained by chemical ionization of $\mathrm{Fe(CO)_5/O_2}$ can be achieved by electron ionization of dicyclopentadienyldinitrosyldiiron $[\mathrm{Cp_2Fe_2(NO)_2}]$.[17]

Results and Discussion

The $\mathrm{Fe}_m\mathrm{O}_n^+$ cations were probed by their collisional activation (CA) mass spectra (Table 1); the results for the mononuclear species $\mathrm{FeO^+}$ and $\mathrm{FeO_2^+}$ are presented for comparative purposes only and are not discussed.[18] While the fragmentation patterns of the $\mathrm{Fe}_m\mathrm{O}_n^+$ clusters appear rather complex at the first inspection, some insightful aspects are revealed if the formal oxidation state of iron is considered as an additional parameter. In this formalism, we assume that oxygen acts as a strict two-electron acceptor, i.e. $\mathrm{O^{2-}}$, count the positive charge as additional valence, and avoid split valencies of the atoms. For example, we assign $\mathrm{Fe_2O^+}$ as containing one $\mathrm{Fe^I}$ and one $\mathrm{Fe^{II}}$; it is thus denoted as $\mathrm{Fe^I/Fe^{II}}$. Accordingly, $\mathrm{Fe_2O_2^+}$ is $\mathrm{Fe^{II}/Fe^{III}}$,

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[a] Institut für Organische Chemie der Technischen
Universität Berlin,
Straße des 17. Juni 135, D-10623 Berlin
Fax: (internat.) + 49-30/314 21102
E-mail: df@www.chem.tu-berlin.de

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Table 1. Representative neutral losses and mass differences (in amu) observed in the CA mass spectra of $Fe_mO_n^+$ clusters formed by CI of $Fe(CO)_5/O_2$ mixtures.

[a][b]	averaged valence[c]	O –16	O_2 –32	Fe –56	FeO –72	FeO_2 –88	FeO_3 –104	Fe_2O_2 –144	Fe_2O_3 –160	Fe_2O_4 –176	Fe_3O_3 –216	Fe_3O_4 –232
FeO^+	3.0	100										
FeO_2^+	5.0[d]	50	100		1							
Fe_2O^+[e]	1.5	60		25	100							
$Fe_2O_2^+$	2.5	100	10	2	8	40						
$Fe_2O_3^+$	3.5	40	100		1	3	5					
$Fe_3O_3^+$	2.33	60	3		100	45	5					
$Fe_3O_4^+$	3.0	100	12		2	20	8			1		
$Fe_4O_4^+$	2.25	5	1		100	5		25	15	5	4	10
$Fe_4O_5^+$	2.75	65	8		2	100	5	8	1			
$Fe_4O_6^+$	3.25	8	100		1	2	15			5		

[a] Formal assignments of the elemental compositions. For example, loss of FeO_3 could also correspond to FeO + O_2, FeO_2 + O, FeO + 2 O etc. – [b] Intensities given relative to the base peaks = 100%. For the sake of clarity, some minor fragments below 5% are omitted. – [c] See text for the formalism. – [d] For discussions of the structural dichotomy of $[Fe,O_2]^{0/+}$, see refs.[18,27]. – [e] Fe_2O^+ is formed in only minor amounts upon CI of $Fe(CO)_5/O_2$ mixtures; $Cp_2Fe_2(NO)_2$ was instead used as precursor.[17]

$Fe_2O_3^+$ is Fe^{III}/Fe^{IV}, $Fe_3O_3^+$ is 2 Fe^{II}/Fe^{III}, etc. The corresponding net oxidation states of the iron atoms in the clusters are 1.5 in Fe_2O^+, 2.5 in $Fe_2O_2^+$, 3.5 in $Fe_2O_3^+$, and 2.3 in $Fe_3O_3^+$.

Using this formalism, the fragmentation patterns can be categorized as follows. (i) For low-valent $Fe_mO_n^+$ clusters ($m/n \geq 1$), losses of FeO prevail, (ii) for $Fe_mO_n^+$ species with $1 > m/n > 2/3$, loss of FeO_2 begins to compete, and (iii) for $Fe_mO_n^+$ ions with $m/n = 2/3$, i.e. $Fe_2O_3^+$ and $Fe_4O_6^+$, loss of molecular oxygen is the dominant pathway. While these patterns can be deduced from Table 1, a more obvious representation is provided by Figure 1, in which only the fractional losses of FeO, FeO_2, and O_2 are considered. Loss of atomic oxygen is not regarded as structurally characteristic and, moreover, it is likely to be overestimated in collisional activation employing kilo electron-volt energies because momentum transfer in high-energy collisions and collection efficiencies favor observation of fragments due to losses of light neutrals.

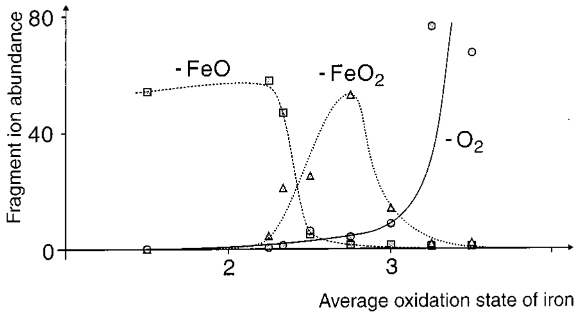


Figure 1. Normalized intensities of FeO (■), FeO_2 (▲), and O_2 (●) losses from $Fe_mO_n^+$ clusters as a function of the averaged oxidation state of the iron atoms; the lines serve just as a guide. Normalization is made to the sum of all fragments observed and the oxidation states are calculated as outlined in the text; for example, a formal oxidation state of 2.5 is attributed to $Fe_2O_2^+$, i.e. Fe^{II}/Fe^{III} that is one Fe^{II} and one Fe^{III}.

Unlike the iron-rich $Fe_mO_n^+$ clusters with $m > n$ studied by Armentrout and co-workers,[7,9] expulsion of neutral iron atoms (or Fe_n aggregates) is rarely observed for the ions under study. Expulsion of FeO units from the low-valent species is formally associated with preservation of the oxidation states of the remaining metal atoms while increasing the average, e.g. loss of the iron(II) compound FeO from $Fe_4O_4^+$ to afford $Fe_3O_3^+$ leads from $3Fe^{II}/Fe^{III}$ to $2Fe^{II}/Fe^{III}$. If we assign neutral FeO_2 to formal iron(IV),[19,20] loss of this neutral corresponds to a disproportionation of the oxidation states between ions and neutrals. In this formalism, losses of molecular oxygen correspond to four-electron reductions of the clusters.

Energetics

The fragmentations observed in the CA spectra cannot directly be related to the associated thermochemical thresholds of the respective channels because collisions occurring in the kilo electronvolt regime do not sample equilibrium. Nevertheless, some correlations can be seen for those clusters for which additional thermochemical information is available.[21]

For example, the predominance of FeO loss from Fe_2O^+ over those of O and Fe, respectively, is consistent with the thermochemistry of the fragments; expressed as sums of heats of formations these are $\Sigma\Delta_fH(Fe^+ + FeO) = 338$ kcal/mol, $\Sigma\Delta_fH(Fe_2^+ + O) = 375$ kcal/mol, and $\Sigma\Delta_fH(FeO^+ + Fe) = 360$ kcal/mol.[21] Similarly, the prevalence of FeO_2 over FeO losses from $Fe_2O_2^+$ is in keeping with the thermochemical thresholds of these channels, i.e. $\Sigma\Delta_fH(FeO^+ + FeO) = 318$ kcal/mol versus $\Sigma\Delta_fH(Fe^+ + FeO_2) = 297$ kcal/mol; note that the base peak due to loss of an O atom has an energy demand of $\Sigma\Delta_fH(Fe_2O^+ + O) = 314$ kcal/mol. Likewise, the competition of FeO and FeO_2 losses for $Fe_3O_3^+$ [Equations (6) and (7)] is consistent with the thermochemical information available. Thus, $D(OFe_2^+–O) \approx D(Fe_2^+–O)$[8] and $D(Fe_2^+–O) = 119 \pm 3$ kcal/mol[7,9] in conjunction with $\Delta_fH(FeO) = 57 \pm 3$ kcal/mol and two nicely consistent values of $\Delta_fH(FeO_2) = 18 \pm 5$ kcal/mol[22] and 15 ± 3 kcal/mol,[3,23,24] respectively, imply $\Sigma\Delta_fH(Fe_2O_2^+ + FeO) = 253$ kcal/mol and $\Sigma\Delta_fH(Fe_2O^+ + FeO_2) = 272$ kcal/mol. Even though the energetics for $Fe_3O_3^+$ are undetermined, these values suggest a difference of about 20 kcal/mol in favor of Equation (6), which is in accord with the observed preference for this channel in the CA spectrum of $Fe_3O_3^+$.

$$Fe_3O_3^+ \rightarrow Fe_2O_2^+ + FeO \qquad (6)$$

$$Fe_3O_3^+ \rightarrow Fe_2O^+ + FeO_2 \qquad (7)$$

$$Fe_3O_3^+ \rightarrow Fe_3O^+ + O_2 \qquad (8)$$

Interestingly, while loss of dioxygen from $Fe_3O_3^+$ according to Equation (8) has a comparable energy demand, $\Sigma\Delta_fH(Fe_3O^+ + O_2) = 269$ kcal/mol, this channel is hardly observed experimentally (Table 1). Hence, the absence (or occurrence) of O_2 loss is subject to kinetic rather than thermodynamic restrictions. Thereby, it could reflect structural motifs of the ionic species being probed. We note in passing that, although conceivable, loss of two O atoms instead of molecular oxygen in Equation (8) is much more energy demanding [$\Sigma\Delta_fH(Fe_3O^+ + 2O) = 387$ kcal/mol]. Thus, sequential oxygen-atom loss is not considered to play a major role in the experimentally observed fragmentation pattern.

Structures

Unambiguous conclusions about the geometric structures of the $Fe_mO_n^+$ clusters cannot be derived from the fragmentation patterns; for example, already eight different isomers need to be considered for the four-atomic, neutral Fe_2O_2 cluster.[25] However, it is precisely the loss of molecular oxygen that at least provides intuitive guides to the possible cluster structures generated. Specifically, intense dioxygen losses observed for oxygen-rich $Fe_2O_3^+$ and $Fe_4O_6^+$ species imply the presence of peroxide units in these clusters while this motif is less likely in the other clusters. Here, the term "peroxide unit" only refers to the presence of O–O bonds in the cluster; whether these are best described as μ^2 peroxo ligands or η^1/η^2 dioxygen complexes is a matter of spin coupling,[18,20,26] which is presently unknown for the cationic $Fe_mO_n^+$ clusters studied here.

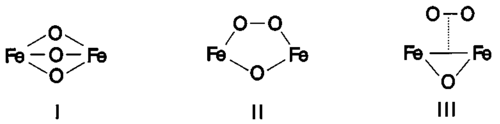
Another, indirect indication of peroxidic structures for $Fe_2O_3^+$ and $Fe_4O_6^+$ is the complete absence of $Fe_3O_5^+$ upon chemical ionization of $Fe(CO)_5/O_2$ mixtures; putative $Fe_3O_5^+$ (250 amu) turns out to be exclusively [$Fe_3O_5H_2^+$] (252 amu) containing one ^{54}Fe isotope; most probably $Fe_3O_4^+\cdot H_2O$. A possible rationale for these observations is that, among the ions formed in the CI plasma, $Fe_2O(CO)^+$ and $Fe_4O_4(CO)^+$, but not $Fe_3O_3(CO)^+$, are observed. These iron oxide carbonyl clusters are in turn likely to serve as precursors for the formation of $Fe_2O_3^+$ and $Fe_4O_6^+$, respectively, by exchange of the CO ligand by dioxygen; a reaction that also occurs for the mononuclear species, i.e. $Fe(CO)^+ + O_2 \rightarrow FeO_2^+ + CO$.[18] Absence of $Fe_3O_3(CO)^+$ as a precursor can account for the failure to generate $Fe_3O_5^+$ in the $Fe(CO)_5/O_2$ plasma. In turn, the presence of O−O bonds in $Fe_2O_3^+$ and $Fe_4O_6^+$ is implied. Thus, we suggest that $Fe_2O_3^+$ is, for example, formed in Equation (9) from an intermediate carbonyl cluster, i.e. the ligand replacement in Equation (9) competes with the oxidation of the cluster according to Equation (5).

$$Fe_2O(CO)^+ + O_2 \rightarrow Fe_2O_3^+ + CO \qquad (9)$$

Oxidation States and Fragmentation Routes

In the series of oxygen-deficient $Fe_mO_n^+$ clusters studied as transients by Armentrout and co-workers,[7,9,10] losses of Fe and Fe_2 units prevailed. In terms of the net oxidation state, these evaporations of neutral Fe units increase the formal cluster valencies, e.g. $Fe_5O_2^+ \rightarrow Fe_3O_2^+ + Fe_2$ leads from an averaged oxidation state of 1.0 in the reactant to 1.67 in the product Fe/O cluster. For the $Fe_mO_n^+$ clusters with $m = n$, our results show preferential losses of the iron(II) compound FeO, e.g. $Fe_3O_3^+ \rightarrow Fe_2O_2^+ + FeO$ corresponds to an increase of the formal valence state from 2.33 in the reactant to 2.5 in the Fe/O cluster formed while the oxidation states of the atoms remain unchanged in reactants and products, i.e. both $2Fe^{II}/Fe^{III}$.

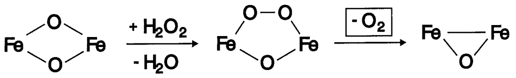
Loss of neutral FeO_2 from the clusters with $m < n$ corresponds to a formal disproportionation of valencies, e.g. from 2.5 in $Fe_2O_2^+$ to 1.0 in the ionic product Fe^+ and 4.0 in neutral FeO_2. Consideration of formal oxidation states also provides a rationale for the switch from FeO to FeO_2 loss upon increasing oxygen content. For example, loss of FeO from $Fe_3O_4^+$ would lead to $Fe_2O_3^+$, which has a high-valent iron(IV) or bearing a peroxidic O−O bond, both features that are considered energetically demanding. Instead, disproportionation with concomitant loss of neutral FeO_2 leads to $Fe_2O_2^+$, an Fe/O cluster with reasonably strong Fe−O bonds.[7–9]



Scheme 1

The oxygen-rich $Fe_mO_n^+$ clusters with $m/n = 2/3$ show preferential losses of molecular oxygen. If these clusters were indeed oxide and not peroxide clusters, high-valent iron(IV) would be present, e.g. Fe^{III}/Fe^{IV} for structure **I** of $Fe_2O_3^+$ (Scheme 1). Involvement of peroxidic structures enables iron to adopt lower oxidation states. For example, the formal valencies in the bridged peroxide **II** are Fe^{II}/Fe^{III} and only Fe^{I}/Fe^{II} in the corresponding dioxygen complex **III**. The avoidance of high valencies is consistent with the mode of generation as well as the fragmentation behavior observed in the experiments. Hence, we suggest that oxygen-rich Fe/O clusters trade-off high oxidation states and prefer the formation of peroxo units instead.

From a conceptual point of view, the formation of peroxo units in the oxygen-rich Fe/O clusters and the associated ability to release molecular oxygen suggest a catalase activity of polynuclear Fe/O clusters. That is, instead of forming high-valent iron-oxo species with hydrogen peroxide, Fe/O clusters can mediate the disproportionation of H_2O_2 into H_2O and 1/2 O_2 via peroxidic metal clusters as intermediates (Scheme 2). In particular, the near degeneracy of low-lying electronic states of different multiplicities in transition metal oxide clusters may counter the spin problem associated with the release of O_2 in its triplet ground state.[27,28] We will continue to address these points in the context of studies of the catalytic activation of peroxides by transition metals in the gas phase.[29,30]



Scheme 2

As demonstrated in this study, collisional activation of cationic Fe/O clusters can provide qualitative insights into structural features, i.e. the presence of O−O bonds, but definitely not more than that. In particular, no precise information about the bonding schemes, e.g. symmetric versus antisymmetric clusters, presence of Fe−Fe bonds, nature of the bridging ligands etc., not to mention spin states, can be discerned. Nevertheless, these kinds of phenomenological studies of transition metal oxide clusters will continue to be important for the time being due to inadequacies of otherwise powerful theoretical methods. While recent applications of density functional theory have proven rather promising for mononuclear iron compounds,[31] there are grave difficulties for these methods in the treatment of coordinatively unsaturated transition metal oxide clusters.[11,12,25]

Experimental Section

The experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration, which has been described elsewhere.[32] The $Fe_mO_n^+$ cations were generated as described above by chemical ionization (CI) of mixtures of $Fe(CO)_5$ and oxygen in ratios varying from ca. 1:5 to 1:50. We note in passing that chemical ionization of mixtures containing high concentrations of oxygen drastically reduces the lifetimes of the tungsten filaments used in the ion source from months (or even years) to a few hours. Better yields of Fe_2O^+ were obtained by electron ionization of $Cp_2Fe_2(NO)_2$.[17] After acceleration to a kinetic energy of 8 keV, the ions of interest were mass-selected using B(1) and E(1) at mass resolutions $m/\Delta m$ between 3000 and 5000. Collisional activation (CA) in the field-free region between E(1) and B(2) was affected using oxygen at 80% transmittance of the incident ion beam. The fragmentation products were scanned using B(2), detected, on-line processed, and accumulated using the AMD/Intectra data system.

An inherent interference for $Fe_mO_n^+$ cations formed upon CI of $Fe(CO)_5/O_2$ mixtures are the carbonyl clusters of the type $Fe_{m-1}(CO)_2O_n^+$, because Fe and 2CO have the same nominal mass (both 56 amu). These interferences are readily apparent as characteristic losses of carbon monoxide (28 amu) in the CA mass spectra, and such losses are not observed for pure $Fe_mO_n^+$ clusters. In practise, these interferences were minimized by appropriate adjustment of the mass resolution whilst maintaining an excess of O_2 in the mixtures, thereby favoring oxidation of all iron-containing ions to the corresponding oxide clusters. Another possible interference is due to clusters in which one ^{56}FeO unit is replaced by an ion-dipole complex with residual water containing the lighter ^{54}Fe isotope (both 72 amu); this interference is readily identified by characteristic loss of water (18 amu) in the CA spectrum of these ions. With the notable exception of formal $Fe_3O_5^+$ (see above), these hydrated iron oxide cluster ions were of negligible abundance.

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