

# Electrospray ionization as a convenient new method for the generation of catalytically active iron-oxide ions in the gas phase

Detlef Schröder<sup>a,b,\*</sup>, Jana Roithová<sup>a</sup>, Helmut Schwarz<sup>b</sup>

<sup>a</sup> Institute of Organic Chemistry and Biochemistry, Flemingovo nám. 2, 16610 Prague, Czech Republic

<sup>b</sup> Institut für Chemie der Technischen Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin, Germany

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## Abstract

Electrospray ionization (ESI) of aqueous iron(III) nitrate solutions can be used as an easy route for the generation of bare iron-oxide and hydroxide cations such as  $\text{FeO}^+$ ,  $\text{FeOH}^+$ , and  $\text{Fe}(\text{OH})_2^+$  in the gas phase. Analysis of the ESI mass spectra obtained under variable conditions in combination with complementary collision experiments suggest that the iron-oxo species are formed by collision-energy driven replacements of nitrate-ligands by water stemming from the sprayed solution. It is demonstrated that the gas-phase reactivity of methane with the iron-oxide cation  $\text{FeO}^+$  generated via ESI is in good agreement with the well-documented literature data for this reaction.

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## 1. Introduction

In 1981, Kappes and Staley [1] reported the first, genuine gas-phase catalysis involving a transition-metal oxide. Thus, it was demonstrated that the iron-oxide cation  $\text{FeO}^+$  reacts with CO to afford  $\text{Fe}^+$  which is then re-oxidized in a second step with  $\text{N}_2\text{O}$  as a reagent (reactions 1 and 2).



In the subsequent research, the  $\text{FeO}^+$  cation was shown to be one of the most powerful oxidants in the gas phase [2,3], capable of even oxidizing methane [4–7]. In extension of the pioneering work of Kappes and Staley, a number of catalytic cycles involving gaseous  $\text{FeO}^+$  have been reported which permit the oxygenation of several hydrocarbons [4,8–13]. In fact,  $\text{FeO}^+$  may be regarded as one of the most carefully investigated transition-metal oxide in the gas phase [3,14]. So far, the generation of  $\text{FeO}^+$  was based on the oxidation of the bare metal cation by  $\text{N}_2\text{O}$  according to reaction (2). Here, we report an

entirely different route for the generation of  $\text{FeO}^+$  via electrospray ionization (ESI [15,16]) of an aqueous  $\text{Fe}(\text{NO}_3)_3$  solution; for earlier reports on the generation of metal-oxide ions using ESI, see [17–19].

## 2. Methods

The measurements were performed using a VG BIO-Q mass spectrometer described elsewhere [20]. Briefly, the VG BIO-Q is a commercial instrument which consists of an ESI source combined with a tandem mass spectrometer of QHQ configuration (Q stands for quadrupole and H for hexapole). In the present experiments, mmolar solutions of  $\text{Fe}(\text{NO}_3)_3$  in distilled water were introduced through a fused-silica capillary to the ESI source via a syringe pump (5–10  $\mu\text{l}/\text{min}$ ). Nitrogen was used as nebulizing and drying gas at a source temperature of 120 °C. For collision-induced dissociation (CID), the ions of interest were mass-selected using Q1, interacted with xenon as a collision gas in the hexapole H under single-collision conditions (typically  $3 \times 10^{-4}$  mbar) at variable collision energies ( $E_{\text{lab}} = 0\text{--}10$  eV), while scanning Q2 to monitor the ionic products. Likewise, ion/molecule reactions were studied by introducing appropriate neutral compounds (i.e., methane as well as  $\text{D}_2\text{O}$ ) in the hexapole collision cell at variable interaction energies; thermal

\* Corresponding author. Tel.: +420 220 183 117; fax: +420 220 183 583.  
E-mail address: [Detlef.Schroeder@uochb.cas.cz](mailto:Detlef.Schroeder@uochb.cas.cz) (D. Schröder).

reactivity was assumed to occur at a collision energy nominally set to  $E_{\text{lab}} = 0$  eV [21–23].

As pointed out previously, the VG Bio-Q does not allow to directly extract quantitative threshold information from CID experiments due to several limitations of the commercial instrument [20]. In the case of weakly bound ions [24], for example, a non-negligible amount of ion decay is observed even at  $E_{\text{lab}} = 0$  eV, which is in part attributed to the presence of collision gas not only in the hexapole, but also in the focusing regions between the mass analyzers. Note that these dissociations do not correspond to metastable ions because they do not occur in the absence of a collision gas. To a first approximation, however, the energy dependence of the product distributions in the CID spectra can be approximated by a sigmoid function [25] which allows some semi-quantitative information about the energetics of the ions to be determined. Here, such an analysis is not pursued any further, however, because the gas-phase thermochemistry of  $\text{FeO}^+$ ,  $\text{FeOH}^+$ ,  $\text{Fe}(\text{OH})_2^+$  is established already reasonably well.

### 3. Results and discussion

Under mild conditions, electrospray ionization of an aqueous solution of  $\text{Fe}(\text{NO}_3)_3$  yields  $\text{Fe}(\text{NO}_3)_2(\text{H}_2\text{O})_n^+$  with  $n$  up to 4 as the leading cationic species. Upon increasingly harsher ESI conditions, subsequent losses of water molecules are observed down to  $n=1$  and 2 (Fig. 1a). When ionization conditions are enforced further, abundant signals due to  $(\text{HO})\text{Fe}(\text{NO}_3)^+$ ,  $(\text{H}_2\text{O})\text{Fe}(\text{NO}_3)^+$ , as well as  $(\text{HO})\text{Fe}(\text{NO}_3)(\text{H}_2\text{O})^+$  are observed (Fig. 1b). Finally, also intense signals corresponding to  $\text{Fe}(\text{OH})_2^+$ ,  $\text{FeOH}^+$ , and  $\text{FeO}^+$  appear (Fig. 1c). As the thermochemical properties and the gas-phase reactivities of these iron cations already were intensively studied [3–9,26–30], here, we focus on the method of ion generation, and in particular on the route which leads from the solvated metal-nitrate ions to the formation of bare metal oxide- and hydroxide cations.

To this end, the major ions formed upon mild ESI conditions were mass-selected and probed by means of collision-induced

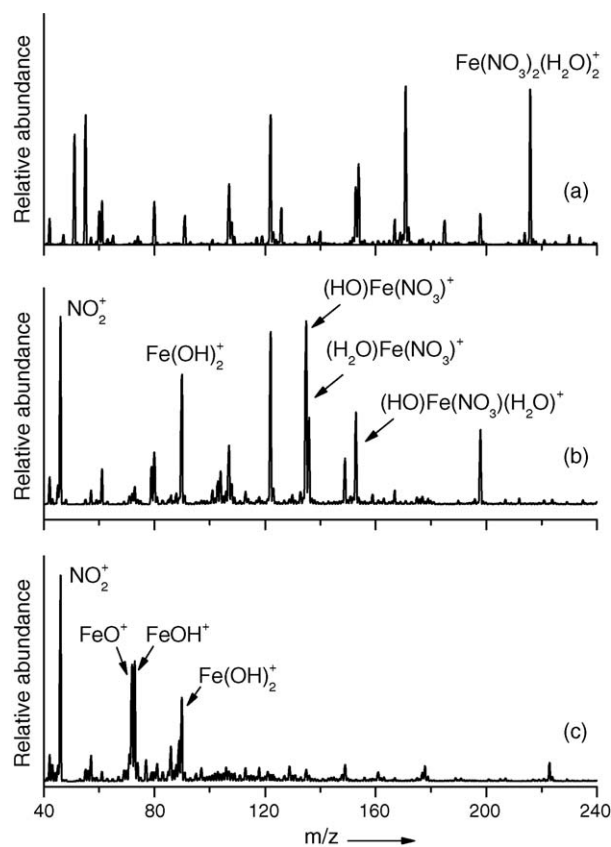


Fig. 1. Representative ESI mass spectra of aqueous  $\text{Fe}(\text{NO}_3)_3$  at cone voltages of (a) 15 V, (b) 30 V and (c) 45 V. The larger the cone voltage, the harsher are the ionization conditions.

dissociation (CID) experiments. For the multiply solvated ions, loss of the solvent molecules largely prevails (Table 1), and the increasing ease of water losses with increasing  $n$  indicates the lower binding energies of the multiply solvated cations [24]. In fact, a considerable amount of CID is even observed at a collision energy nominally set to 0 eV indicating that the water binding energies of the larger hydrated ions are in the order of magnitude of their respective internal energy content. In the case of

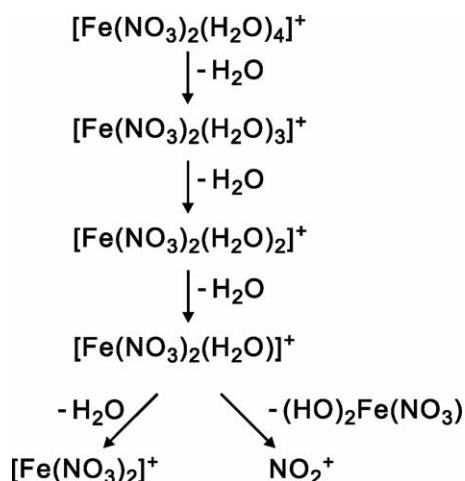
Table 1  
Major fragments in the CID mass spectra of mass-selected  $\text{Fe}(\text{NO}_3)_2(\text{H}_2\text{O})_n^+$  cations at three different collision energies ( $E_{\text{lab}}$  in eV)<sup>a</sup>

$n$	$E_{\text{lab}}$	$M^{+\text{b}}$	$-\text{H}_2\text{O}$	$-2 \text{H}_2\text{O}$	$-3 \text{H}_2\text{O}$	$-\text{HNO}_3$	$\text{NO}_2^+$
	0	85	100	20			
4	5	55	60	100	15		1
	10	35	30	75	100	3 <sup>c</sup>	25
	0	100	75	6			
3	5	48	100	60			2
	10	70	60	100	4	8 <sup>c</sup>	30
	0	100	20				
2	5	50	100				15
	10	55	35	4		4	100
	0	100					4
1	5	70	4				100
	10	50	4			2	100

<sup>a</sup> Given relative to the base peak (100%). Note that some dissociation at a collision energy set to nominally  $E_{\text{lab}} = 0$  eV is observed for weakly bounded complexes in the multiple set-up (see experimental details).

<sup>b</sup>  $M^+$  denotes the mass-selected parent ion in the CID experiment.

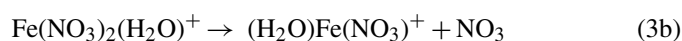
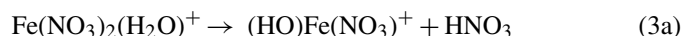
<sup>c</sup> Here, this entry corresponds to the sum of combined  $\text{HNO}_3 + n\text{H}_2\text{O}$  losses.



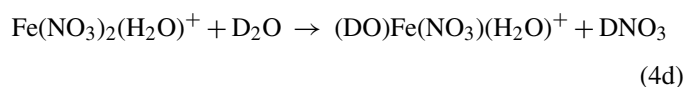
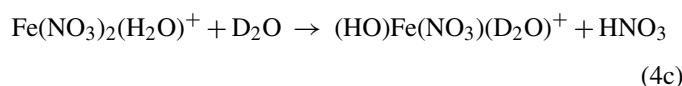
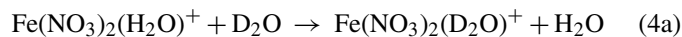
Scheme 1.

$\text{Fe}(\text{NO}_3)_2(\text{H}_2\text{O})^+$ , however, loss of water is a very minor process, whereas the major channel leads to  $\text{NO}_2^+$  along with the putative formation of neutral  $(\text{HO})_2\text{Fe}(\text{NO}_3)$ . The fact that the resulting cation  $\text{NO}_2^+$  is metal-free can be appreciated considering the large ionization energies of gaseous  $\text{Fe}^{\text{III}}$  compounds, e.g.,  $\text{IE}(\text{FeCl}_3) = 10.9 \text{ eV}$  [31]. From the results, a rationale for the consecutive fragmentations of  $\text{Fe}(\text{NO}_3)_2(\text{H}_2\text{O})_n^+$  can be proposed (Scheme 1); note that CID data for bare, unsolvated  $\text{Fe}(\text{NO}_3)_2^+$  cannot be provided because only traces of this ion are directly formed in the ESI source.

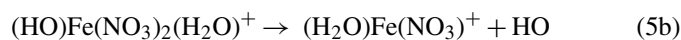
The most important finding within the present context is, however, that the protolysis of the monosolvated complex according to reaction (3a) is almost negligible upon CID with xenon, whereas  $(\text{HO})\text{Fe}(\text{NO}_3)^+$  represents one of the major ions directly emerging from the ion source under medium conditions of ionization [32].



Accordingly, it is proposed that the species  $(\text{HO})\text{Fe}(\text{NO}_3)^+$  is formed via endothermic ion/molecule reactions in the source region with water molecules stemming from the spray solvent acting as a collision gas, thereby favoring protolysis, rather than CID. The same conditions appear to also favor reduction of the iron(III) species to the formal iron(II) compound  $(\text{H}_2\text{O})\text{Fe}(\text{NO}_3)^+$ , which involves a formal reduction to iron(II) concomitant with loss of an  $\text{NO}_3$  radical (reaction 3b).



In order to probe this hypothesis, mass-selected  $\text{Fe}(\text{NO}_3)_2(\text{H}_2\text{O})_n^+$  ions were reacted with  $\text{D}_2\text{O}$  introduced to the hexapole collision cell at variable interaction energies. At a collision energy nominally set to 0 eV, degenerate exchange of the  $\text{H}_2\text{O}$  ligand(s) against  $\text{D}_2\text{O}$  largely predominates for all  $\text{Fe}(\text{NO}_3)_2(\text{H}_2\text{O})_n^+$  ions. We note further that the amount of interligand H/D exchange is negligible (i.e., the fraction of HDO complexes is small and coincides with the actual degree of deuteration of the water present in the collision cell). This finding accordingly implies that the water ligands in the  $\text{Fe}(\text{NO}_3)_2(\text{H}_2\text{O})_n^+$  cations are intact and that isomeric structures such as  $(\text{HO})\text{Fe}(\text{NO}_3)(\text{HNO}_3)(\text{H}_2\text{O})_{n-1}^+$  do not play a significant role; for a counter-example with quite similar iron cations, see [33]. With respect to  $n = 1$ , reaction (4a) comprises ca. 90% of all products. In addition, some amount of association takes place even at only  $10^{-4}$  mbar (reaction 4b, ca. 7% of all products). Most significant in the present context of iron-oxide formation is, however, the expulsion of neutral  $\text{XNO}_3$  according to reactions (4c) and (4d) which is observed to occur to a small extent in the case of  $n = 1$ . The resulting product ions can then either lose water or a hydroxy radical (reaction 5), thereby accounting for the cations  $(\text{HO})\text{Fe}(\text{NO}_3)^+$  and  $(\text{H}_2\text{O})\text{Fe}(\text{NO}_3)^+$  as observed in Fig. 1b.



With regard to the generation of these iron-hydroxo species it is noteworthy that the branching ratio of the  $\text{XNO}_3$  losses significantly increases at elevated collision energies (Fig. 2). This result lends credit to our working hypothesis that the  $(\text{HO})\text{Fe}(\text{NO}_3)(\text{H}_2\text{O})_n^+$  species with  $n = 0-2$  emerging from the ion source are formed in collision-energy driven anion-exchange reaction in the source region, where considerable amounts of the solvent vapor are still present.

Upon CID of mass-selected  $(\text{HO})\text{Fe}(\text{NO}_3)^+$  with xenon, the metal-free cations  $\text{NO}_2^+$  and  $\text{NO}^+$  are observed as major fragments, whereas iron-containing ions such as  $\text{FeOH}^+$  and  $\text{OFeOH}^+$  are of minor abundance (Fig. 3a). Thus, also the  $(\text{HO})\text{Fe}(\text{NO}_3)^+$  species does not appear as an obvious intermedi-

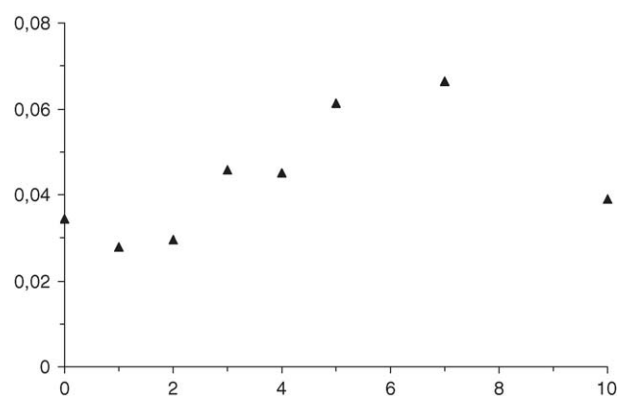


Fig. 2. Branching ratio of  $\text{XNO}_3$  losses ( $\text{X} = \text{H}, \text{D}$ ) upon reaction of mass-selected  $\text{Fe}(\text{NO}_3)_2(\text{H}_2\text{O})^+$  with gaseous  $\text{D}_2\text{O}$  as a function of collision energy ( $E_{\text{lab}}$ ).

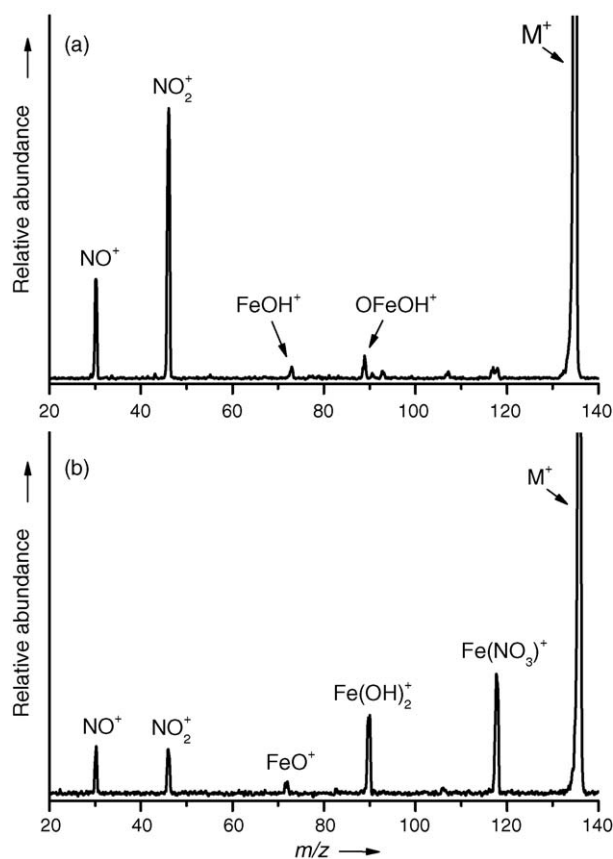


Fig. 3. CID spectra of (a) mass-selected  $(\text{HO})\text{Fe}(\text{NO}_3)^+$  (top) and (b) mass-selected  $(\text{H}_2\text{O})\text{Fe}(\text{NO}_3)^+$  (bottom). In both cases, the collision energy was adjusted to  $E_{\text{lab}} = 10 \text{ eV}$  and the parent ions  $M^+$  are off-scale by a factor of 2.

ate en route to the generation of the ions  $\text{Fe}(\text{OH})_2^+$ ,  $\text{FeOH}^+$ , and  $\text{FeO}^+$  under ESI conditions (Fig. 1). Instead, the CID spectrum of mass-selected  $(\text{H}_2\text{O})\text{Fe}(\text{NO}_3)^+$  shows a reasonably intense signal due to  $\text{Fe}(\text{OH})_2^+$  concomitant with loss of neutral  $\text{NO}_2$  (Fig. 3b). From the latter cation, both  $\text{FeO}^+$  as well as  $\text{FeOH}^+$  are accessible via CID, and the energy-dependence of the fragment ions (Fig. 4) is perfectly consistent with literature data [28–30].

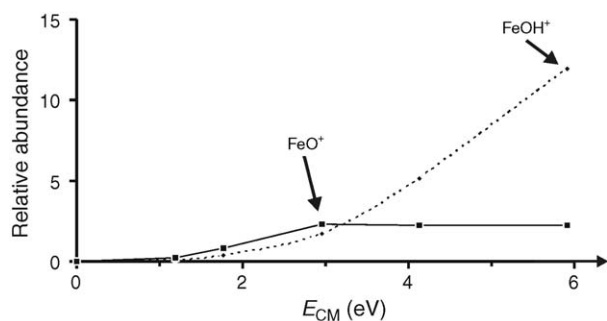


Fig. 4. Relative abundances (intensities normalized to a sum of 100 including the parent ion) of the fragment ions  $\text{FeO}^+$  and  $\text{FeOH}^+$  upon CID of mass-selected  $\text{Fe}(\text{OH})_2^+$  at various collision energies.

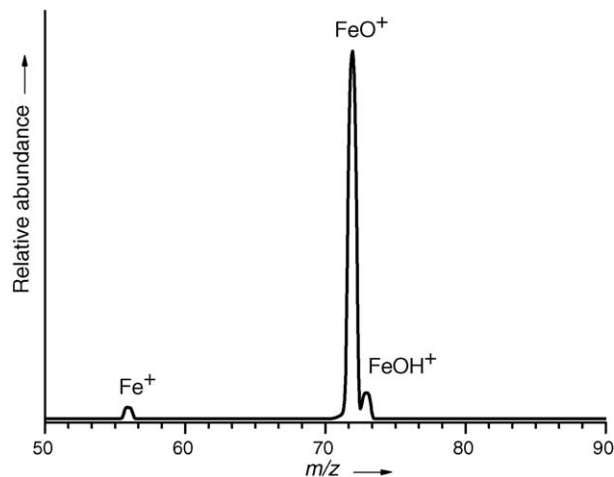


Fig. 5. Ion/molecule reaction of mass-selected  $\text{FeO}^+$  generated via ESI with methane at a collision energy nominally adjusted to  $E_{\text{lab}} = 0 \text{ eV}$  and a methane pressure of  $3 \times 10^{-4} \text{ mbar}$ .

It can accordingly be concluded that the  $[\text{FeO}_2\text{H}_2]^+$  ion formed upon ESI corresponds to the energetically more stable dihydroxide  $\text{Fe}(\text{OH})_2^+$ , rather than the hydrated metal-oxide cation  $(\text{H}_2\text{O})\text{FeO}^+$ . From the dihydroxide cation, loss of water to afford  $\text{FeO}^+$  (reaction 6a) is hence less energy demanding than loss of an  $\text{HO}^\bullet$  radical to yield  $\text{FeOH}^+$  (reaction 6b), yet the latter channel is entropically favored. Accordingly,  $\text{FeO}^+$  as a fragment ion stemming from  $\text{Fe}(\text{OH})_2^+$  is already observed at low collision energies, but once  $\text{FeOH}^+$  formation becomes energetically accessible, it begins to predominate because it does not require a hydrogen migration [28,30].

Hence, the route for the formation of the title ions upon more drastic ESI conditions is in fact quite complex. After initial desolvation of  $\text{Fe}(\text{NO}_3)_2(\text{H}_2\text{O})_n^+$ , a collision-induced reaction with water stemming from the spray leads to the formal iron(II) compound  $(\text{H}_2\text{O})\text{Fe}(\text{NO}_3)^+$  from which a  $\text{NO}_2^\bullet$  radical is lost, to again afford the iron(III) compound  $\text{Fe}(\text{OH})_2^+$ , which then serves as a precursor for  $\text{FeO}^+$  and  $\text{FeOH}^+$ .

Finally, the reactivity of the ions generated via ESI is addressed briefly in order to demonstrate the usefulness of this rather simple method of ion generation. To this end, mass-selected  $\text{FeO}^+$  was allowed to react with methane in the hexapole collision cell and the product ions formed were detected by scanning the next mass analyzer. Fig. 5 shows the ionic products  $\text{Fe}^+$  and  $\text{FeOH}^+$  in a branching ratio of  $(31 \pm 4) : (69 \pm 4)$ ; this finding nicely matches previous data on this reaction, which belongs to one of most carefully studied reactions of gaseous transition-metal ions. Thus, using an ion-beam set-up similar to that used here, a ratio of 29:71 was obtained, ion-cyclotron measurements led to 39:61, whereas experiments conducted at significantly higher pressure in a selected ion-flow tube gave 82:18; the latter effect has been attributed to the particular shape of the potential-energy surface of the overall reaction [7]. In this context, we note in passing that also a trace amount of  $\text{FeCH}_2^+$  is observed as ionic product (too small to be seen in Fig. 5), again fully consistent with the previous reports [4,7].

While absolute rate constants cannot be determined easily in a multipole set-up, calibration of the  $\text{FeO}^+ + \text{CH}_4$  reaction with the well-known reaction of bare  $\text{Pt}^+$  with methane [34] gives a rate constant of  $k = (9 \pm 2) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  for the reaction of  $\text{FeO}^+$  which matches quite well within the experimental errors with the literature values [7]. Finally, we investigated, whether or not the bimolecular reaction of diatomic  $\text{FeO}^+$  with methane depends on the conditions under which the precursor cation is formed upon ESI. However, within the range of cone voltages at which sufficient yields of  $\text{FeO}^+$  are achievable, no notable changes in the bimolecular reactivity of mass-selected  $\text{FeO}^+$  were found. At the first glance, this finding may appear as a contradiction because elevated cone voltages obviously enhance fragmentation and hence increase the energy content of the ions emerging from the ESI source. Quite specifically, this is even reflected for diatomic  $\text{FeO}^+$  cation itself which vanishes at cone voltages above  $U_C = 100 \text{ V}$  due to fragmentation to bare  $\text{Fe}^+$ . Moreover, clear correlations between energy content and the conditions in the ESI source have been reported for several large molecules [35]. Nevertheless, it is to be recognized that the cone region is still located in the high pressure regime of the ESI source and non-negligible time elapses before actually probing ion-reactivity in the hexapole collision cell. By analogy to arguments put forward by Chen and co-workers [36], we therefore attribute the absence of an influence of the cone voltage in the ESI source on the reactivity of mass-selected  $\text{FeO}^+$  in the hexapole collision cell to the limited number of degrees of freedom of a diatomic molecule in conjunction with the considerable amount of collision cooling occurring during the transfer from the high-pressure region of the cone to the ultra-high vacuum of the mass analyzer.

#### 4. Conclusions

Electrospray mass spectrometry is shown to serve as a simple method for the generation of iron-oxide species such as  $\text{FeO}^+$ ,  $\text{FeOH}^+$ , and  $\text{Fe}(\text{OH})_2^+$  in reasonable yields. Accordingly, the same technique might also be applicable for the generation of other reactive metal-oxide ions which have so far escaped further reactivity studies due to the difficulties encountered in ion generation [37,38]. In this respect, ESI provides an alternative which prevents many of the problems inherent to other approaches. A key requisite is the use of pure water as a solvent, because all other solvents suitable for ESI are oxidized themselves by the high-reactive iron ions. Despite its simplicity, this method for ion generation via ESI is therefore limited to those instruments which can also be operated with pure water [39].

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