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Solvent and Ligand Effects on the Structures of Iron Halide Cations in the Gas Phase

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The effects of the oxidation state, the ligand, and the solvent on structures and energetics of cationic iron complexes are investigated by means of electrospray-ionization mass spectrometry. Insights into the potential-energy surfaces of FeX^+, FeX_2^+, and $XFe(OCH_3)^+$ ions (X = F, Cl, Br, I) with a variable number of coordinated methanol molecules are obtained by means of collision experiments and complementary thermochemical considerations. It is shown that upon change of the halide ligand, the weakly solvated ions respond differentially to the increasing need for stabilization of the partial charge on the metal center. For example, whereas $F_2Fe(CH_3OH)_n^+$ ions tend to lose mainly HF for n = 1–3, the loss of HBr is not observed at all for $Br_2Fe(CH_3OH)_n^+$. Instead, the iron-bromide cations undergo reductive loss of atomic bromine. $Cl_2Fe(CH_3OH)_n^+$ bears an intermediate position in that both reduction as well as elimination of HCl can occur.

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Introduction

One important factor for the success of mass spectrometry as a tool for investigating the elementary steps of various catalytic reactions is its ability to design and to probe model systems of variable complexity. Many experiments focus exclusively on the intrinsic properties of reactive centers by studying isolated, ligand-free atomic metal ions or their clusters, and the knowledge that has been accumulated for these systems is rather astonishing.[1] More complex systems have also been addressed, even including consideration of extrinsic factors such as ligands and counterions.[2–5] While investigations of gaseous metal clusters can largely assist in bridging the gap between gas-phase reactions and heterogeneous catalysis, understanding the often crucial role of the solvent is necessary in order to translate gas-phase chemistry data to processes taking place in solution. Different approaches have been pursued in order to include solvent molecules in mass spectrometry.[6–9] The unique features of electrospray ionization (ESI)[10,11] mass spectrometry allow the straightforward generation of a large number of solvated ions.[3,4,12–15] Here, we report a systematic study of the cationic complexes formed upon ESI of methanolic solutions of FeX_2 (X = F, Cl, Br, I) and FeX_3 (X = F, Cl, Br). Iron was investigated because of its growing importance in the field of catalysis[16] and biochemistry.[17] Halides were chosen because of their sufficient solubility in organic solvents,[18] which is reflected in their frequent use as catalysts and, additionally, they permit the investigation of periodic trends regarding the role of ligands. Methanol was used for its excellent performance as an ESI solvent and furthermore because it allows for various types of solvation mechanisms, like mere association, solvolysis, hydrogen bonding, etc. and, moreover, also has a potential for bond activation processes.[15]

Results and Discussion

FeX_2 (X = F, Cl, Br, I): In general, two different types of mononuclear ions are formed upon ESI of methanolic FeX_2 solutions: $XFe(CH_3OH)_n^+$ with $n \leq 5$ and $Fe(OCH_3)(CH_3OH)_n^+$ with $n \leq 3$. In addition, iron clusters of the formal composition $(Fe_mX_{2m-1})(CH_3OH)_n^+$ are formed, in which m can reach numbers of up to six and n up to eight. Reduced clusters of the type $(Fe_mX_{2m-2})(CH_3OH)_n^+$ are only observed for the heavy halogens, i.e. bromine and iodine. Here, we focus on the mononuclear $XFe(CH_3OH)_n^+$ ions. At very low cone voltage (≈0 V), which corresponds to rather mild ionization conditions, multiply solvated complexes $XFe(CH_3OH)_n^+$ with n = 3–5 are formed. With rising cone voltage (30–50 V), the ions lose their weakly bound solvent molecules, and $XFe(CH_3OH)_n^+$ ions with n = 0–3 dominate the spectra. Under these conditions, also $Fe(OCH_3)(CH_3OH)_n^+$ ions with n = 0–3 are observed in substantial quantities. At very high cone voltages, the complexes undergo consecutive fragmentation and are finally reduced to bare atomic iron(I) Fe^+.

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Qualitative insight into the potential-energy surfaces of the solvated iron(II)halide cations and estimations of the binding energies to the solvent molecules are achieved by means of collision-induced dissociation (CID) experiments (Table 1). The exclusive exit channel for $XFe(CH_3OH)_n^+$ cations with $n = 3$–5 corresponds to the loss of an intact methanol solvent molecule. For $n = 4$ and 5, the methanol ligands are that weakly bound that they are already lost at thermal energies; accordingly, the determination of *AEs* is not reasonable anymore, because it would result in negative values. The findings for $n = 1$–3 reveal two trends. First, the binding energies between the metal core and the solvent molecule appear to decrease with increasing solvation. Obviously, the partial charge on the metal center is effectively stabilized by the first methanol molecules, so that additional solvation accompanied by increased steric hindrance becomes less and less significant. Secondly, the binding energies decrease from fluorine to bromine, which can be attributed to the fact that the more electronegative fluorine induces a much higher charge on the metal center than bromine. For $n = 0$–2 in the case of X = Cl, Br and $n = 0$, 1 in the case of X = F, the reductive loss of a halogen atom is available as an additional fragmentation channel. Given the qualitative nature of the *AE* measurements, we note in passing that the experimental values for the unsolvated species are in rather good agreement with values reported in the literature (FeF^+: 4.5; $FeCl^+$: 3.5; $FeBr^+$: 2.7; FeI^+: 2.6 eV).[19–23] Further, the binding energies for the cleavage of the Fe–X-bonds also increase with solvation, the origin of which has been discussed previously.[15]

If solvated with only one or two methanol molecules, the $FFe(CH_3OH)_n^+$ ions exhibit elimination of HF as yet another fragmentation channel. Consequently, the mere description of the complex as a FeF^+ core to which the solvent molecules are coordinated seems insufficient, because direct loss of HF from such a structure is considered less likely compared to the loss of the coordinated methanol ligand. Instead, a rearrangement according to Reaction (1) must take place prior to fragmentation.

$$FFe(CH_3OH)_n^+ \rightleftharpoons (HF)Fe(OCH_3)(CH_3OH)_{(n-1)}^+ \quad (1)$$

The breakdown graph (Figure 1) for the CID fragments of mass-selected $FFe(CH_3OH)^+$ provides some further insight into the potential-energy surface of this system. The loss of HF bears the lowest appearance energy of about 0.5 eV and shows a characteristic increase in intensity, reaching a maximum at about E_{CM} = 2 eV, and then declines at higher collision energies, whereas the loss of methanol increases until about E_{CM} = 5 eV. This kind of behavior points to the operation of a kinetic hindrance, i.e. the presence of the two isomers $FFe(CH_3OH)^+$ and $(HF)Fe(OCH_3)^+$ separated by a barrier that is of comparable height as the appearance energy for the elimination of HF. On the basis of thermochemical considerations, $FFe(CH_3OH)^+$ is indicated to be more stable than $(HF)Fe(OCH_3)^+$ (see Appendix). However, the loss of HF represents the energetically lowest-lying exit channel. At low collision energies, the system will accordingly rearrange and dissociate to the $Fe(OCH_3)^+$ fragment. Once direct loss of methanol is energetically accessible at about 1.6 eV, this route of fragmentation is preferred, since the density of states for the direct bond cleavage resulting in two molecules is orders of magnitude higher than the density of states for the tight transition state connecting the two tautomers. For a detailed discussion, including DFT calculations, of the related $Cl_2Fe(CH_3OH)^+$/$ClFe(HCl)(OCH_3)^+$ system, see ref.[15]

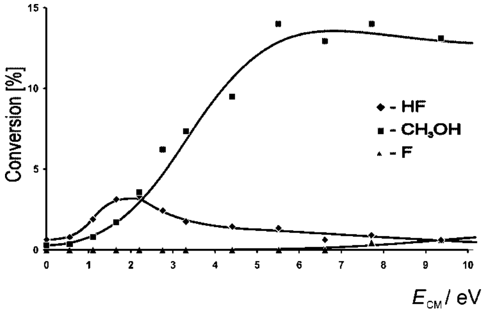

Figure 1. Breakdown graph of the CID fragments of mass-selected $FFe(CH_3OH)^+$ as a function of collision energy in the center of mass frame.

FeX_3 (X = F, Cl, Br): Three different iron(III) species are formed upon ESI of methanolic FeX_3 solutions: $X_2Fe(CH_3OH)_n^+$, $XFe(OCH_3)(CH_3OH)_n^+$, and $Fe(OCH_3)_2(CH_3OH)_n^+$, with n up to five. In addition, some reduced ions are observed, namely, the iron(II)cations $XFe(CH_3OH)_n^+$ and $Fe(OCH_3)(CH_3OH)_n^+$ as well as the formal iron(I) clusters $Fe(CH_3OH)_n^+$. The spectra also show the presence of small amounts of binuclear clusters of the formal compositions $Fe_2X_m(CH_3OH)_n^+$ ($m = 3$–5, $n = 0$–4). At low cone voltages, ESI produces by and large the same type of solvated FeX_2^+ cations from all three solutions of FeF_3, $FeCl_3$, and $FeBr_3$ in methanol, respectively. How-

Table 1. Phenomenological appearance energies [eV] for the losses of CH_3OH as well as X upon CID of mass-selected $XFe(CH_3OH)_n^+$ ions (X = F, Cl, Br, I).

$XFe(CH_3OH)_n^+$	*AE* [eV] (-CH_3OH)				*AE* [eV] (-X)			
n vs. X	F	Cl	Br	I	F	Cl	Br	I
0					5.2 ± 0.9	3.7 ± 0.4	3.2 ± 0.6	2.3 ± 0.6
1	1.6 ± 0.2	1.6 ± 0.2	1.1 ± 0.2	1.1 ± 0.2	7 ± 1	5.4 ± 0.5	5.3 ± 0.4	4.7 ± 0.6
2	0.9 ± 0.2	0.8 ± 0.2	0.5 ± 0.2	0.6 ± 0.2		6.5 ± 0.9	6.6 ± 0.8	6.5 ± 0.5
3	0.4 ± 0.2	0.1 ± 0.1	0.2 ± 0.2	0.1 ± 0.1				

ever, the similarities vanish once solvation decreases. Hence, the need for stabilization of the partial charge on the metal center is even larger than in the case of the iron(II) compounds. Generally, the ions react in two different ways. The first route corresponds to the elimination of HX resulting in new iron(III) complexes; this pathway is mainly observed for X = F. Alternatively, reductive loss of a halogen atom takes place, which dominates in the case of $FeBr_2^+$ ions. Obviously, there exist substantial differences in the respective potential-energy surfaces regarding the rearrangement/dissociation energy requirements between the two tautomers $X_2Fe(CH_3OH)_n^+$ and $XFe(OCH_3)(HX)(CH_3OH)_{(n-1)}^+$.

All appearance energies for the elimination of methanol from the solvated iron(III) halide cations are larger than those of the corresponding iron(II) species (Table 2 vs. Table 1). This finding can be attributed to the increased partial charge of the metal center, which hence leads to a larger ion-dipole interaction between the metal center and the methanol molecules and thus increased binding energies of the ligands.

Loss of HF from the complexes $F_2Fe(CH_3OH)_n^+$ (n = 1–3) is observed with rather low *AEs* of 0.5 eV, hence suggesting that hydrogen migrations to form the tautomeric ions $FFe(OCH_3)(HF)(CH_3OH)_{(n-1)}^+$ are facile. Evaporations of hydrogen chloride are observed for $Cl_2Fe(CH_3OH)_n^+$ (n = 1, 2). Here, the importance of the oxidation state of the metal becomes evident, for HCl elimination has not been detected for any solvated iron(II) chloride cation. Just like in the case of HF elimination, the *AE*s for the loss of HCl from $Cl_2Fe(CH_3OH)_n^+$ (n = 1, 2) do not change much with the degree of solvation, which can be attributed to the operation of two opposing effects. On the one hand, the partial charge on the metal center is lowered with increasing solvation as discussed above, and accordingly the binding energy to HX, which is based mainly on ion-dipole interaction, decreases. On the other hand, the hydrogen migration, which is crucial for formation of HX, may be favored upon increasing solvation, because the ligands are brought to closer vicinity. The cations $F_2Fe(CH_3OH)_n^+$ (n = 0, 1) and $X_2Fe(CH_3OH)_n^+$ (X = Cl, Br; n = 0–2) exhibit loss of a halogen atom as an additional fragmentation channel, which formally corresponds to a reduction of the oxidation state of the metal. In fact, for all iron(III)-bromide cations the reduction of the metal via elimination of a halogen atom completely suppresses the formation of HX via hydrogen rearrangement. The appearance energies for the dissociation of the XFe^+–X-bond of the naked species seem to be somewhat lower compared with existing literature values [$D_o(ClFe^+–Cl$ = 2.19; 2.53)].[21,24,25] Interestingly, the trend of binding energy of the metal-halide bond responds differently to a changing degree of solvation. Whereas with coordination of the first methanol molecule the *AE* for the loss of fluorine increases by as much as 1.4 eV, it changes only by 0.8 and 0.1 eV for the ejection of chlorine and bromine atoms, respectively (Table 2).

Figure 2 shows the breakdown graphs for the CID fragments of mass-selected $X_2Fe(CH_3OH)^+$ ions (X = F, Cl,

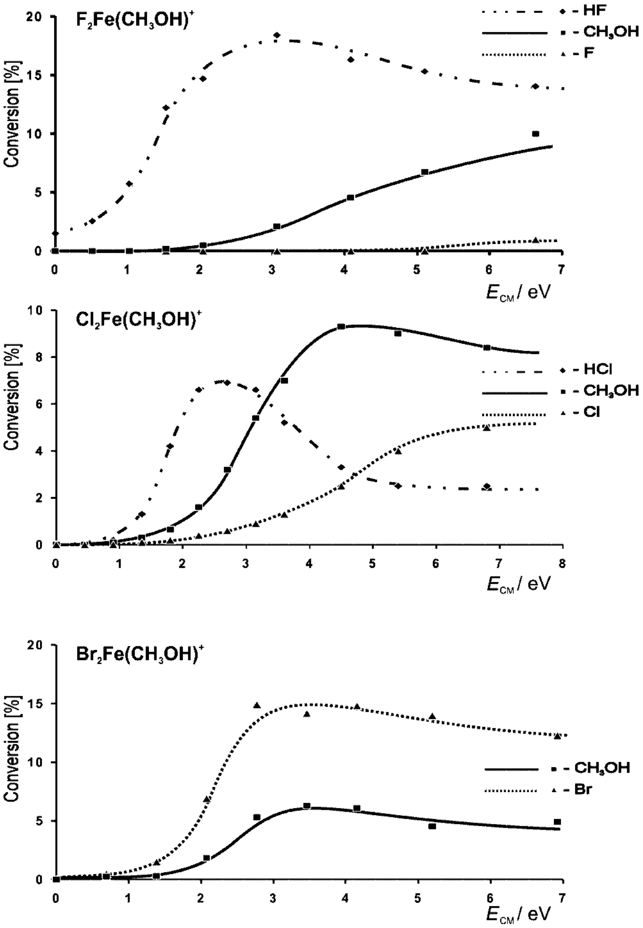

Figure 2. Breakdown graphs of the CID fragments of mass-selected $X_2Fe(CH_3OH)^+$ cations as a function of collision energy in the center of mass frame.

Table 2. Phenomenological appearance energies [eV] for the losses of CH_3OH, X, and HX upon CID of mass-selected $X_2Fe(CH_3OH)_n^+$ ions.

$XFe(CH_3OH)_n^+$	*AE* [eV] (-CH_3OH)			*AE* [eV] (-X)		*AE* [eV] (-HX)		
n vs. X	F	Cl	Br	F	Cl	Br	F	Cl
0				1.8 ± 0.3	1.6 ± 0.3	1.4 ± 0.3		
1	2.2 ± 0.3	1.9 ± 0.2	1.6 ± 0.3	3.2 ± 0.2	2.4 ± 0.5	1.5 ± 0.4	0.5 ± 0.2	1.2 ± 0.1
2	1.5 ± 0.2	1.3 ± 0.1	0.8 ± 0.2		3.0 ± 0.5	2.5 ± 0.5	0.5 ± 0.2	1.0 ± 0.1
3	0.5 ± 0.2	0.4 ± 0.2	0.2 ± 0.1				0.5 ± 0.2	
4	<0.5	0.3 ± 0.2	<0.2					
5	<0.5	<0.3	<0.2					

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Br), and the influence of the halide becomes quite evident upon comparison. For X = F, elimination of HF corresponds to the dominant fragmentation channel with the lowest *AE* and the largest intensity, while evaporation of the solvent exhibits a higher *AE* as well as a lower intensity. Reductive loss of the fluorine atom is negligible over the whole energy regime studied. In the case of X = Cl, the energy behavior reveals a kinetic hindrance of HCl elimination, which still exhibits the lowest *AE* and thus is the most intense fragmentation channel at low collision energies, but becomes less pronounced than evaporation of the solvent at collision energies above 3.3 eV and even less intense than the reductive elimination of atomic chlorine at collision energies above 5 eV. For X = Br, reductive cleavage of the Fe–X-bond even dominates over the loss of the solvent both in terms of appearance energy and intensity.

The assumption that the $X_2Fe(CH_3OH)^+$ isomer is more stable than $XFe(OCH_3)(HX)^+$ implies qualitative potential-energy surfaces for the competing losses of CH_3OH, X, and HX as depicted in Figure 3.

On the very left, the energies of the $XFe(CH_3OH)^+$ cation and the halogen radical as well as the naked FeX_2^+ cation and the free methanol molecule are shown. The binding energy of the radical to the iron(II) species ΔE_1 and the binding energy of the solvent molecule to the iron(III) halide cation ΔE_2 are assumed to correspond to the *AEs* for the reductive loss of the halogen and the elimination of methanol, respectively. As discussed above for X = F and Cl, the barrier separating the tautomers (ΔE_3) has to be smaller or of comparable height than that of the exit channel for the loss of HX (ΔE_5). Finally, the stability difference of the isomers **A** and **B** (ΔE_4) can be derived by estimations based on Equation (2) and Equation (3), where the key parameters are the changes of Fe-X and H-X binding energies (for details, see Appendix).

$$\Delta_f H(X_2Fe(CH_3OH)^+) = \Delta_f H(FeX_2^{\ +}) + \Delta_f H(CH_3OH) - BDE(X_2Fe^+ - (CH_3OH)) \qquad (2)$$

$$\Delta_f H(XFe(OCH_3)(HX)^+) = \Delta_f H(XFe(OCH_3)^+) + \Delta_f H(HX) - BDE((OCH_3)XFe^+ - (HX)) \qquad (3)$$

Using an approach analogous to that described above for the iron(II) species (also see Appendix), some semi-quantitative estimates can be made for the energy differences ΔE_1–ΔE_5, and the results are summarized in Table 3.

Table 3. Energy differences ΔE_1 to ΔE_5 [eV] (as defined in Figure 3) for the competing losses of methanol, HX, and X from cationic $X_2Fe(CH_3OH)^+$ complexes (X = F, Cl, Br).[a]

	F	Cl_{exp}	Cl_{theo}	Br
ΔE_1	3.2	2.4		1.5
ΔE_2	2.2	1.9	1.93	1.6
ΔE_3	<0.5	<1.2	1.35	>0.83
ΔE_4	<0.5	<1.2	0.83	>0.83
ΔE_5	0.5	1.2	1.40	–[b]

[a] In the estimation of the values for X = F and Cl_{exp}, thermodynamic control is assumed. The values of Cl_{theo} are taken from theoretical data given in ref.[15]. [b] Loss of HBr is not observed experimentally.

From the CID experiments alone it cannot be deduced, whether the *AE* of HX elimination is determined by the energy demand of the exit channel (Case **a** in Figure 3), hence the fragmentation is thermodynamically controlled, or if the height of the barrier is crucial (Case **b** in Figure 3) such that the fragmentation is subject to kinetic control.[26] For the system $Cl_2Fe(CH_3OH)^+$, computational results have demonstrated that the fragmentation is subject to thermodynamic control.[15]

Iron(III) alkoxide ions $XFe(OCH_3)(CH_3OH)_n^{\ +}$ are formally accessible from $X_2Fe(CH_3OH)_{n+1}^{\ +}$ via loss of HX according to Equation (4).

$$X_2Fe(CH_3OH)_{n+1}^{\ +} \rightleftharpoons XFe(OCH_3)(CH_3OH)_n^{\ +} + HX \qquad (4)$$

In this respect, the maximum number of coordinated solvent molecules gives a hint, whether the reaction has already taken place in solution or if it occurs only in the ESI process after evaporation. Multiply solvated ions, already present in solution, should appear at the mildest ionization conditions, whereas ions formed via collisional activation in the mass spectrometer should only be produced under more drastic ESI conditions.

For X = F, $FFe(OCH_3)^+$ cations are observed with one or two solvent molecules attached to it. Keeping in mind that solvated FeF_2^+ ions lose HF unless more than three methanol molecules are coordinated, this is exactly the result expected for ion formation in the evaporation process. The same holds true for the $ClFe(OCH_3)^+$ ions. Only iron(III) bromide cations never lose HBr in CID experiments, and yet, $BrFe(OCH_3)^+$ ions with up to four coordi-

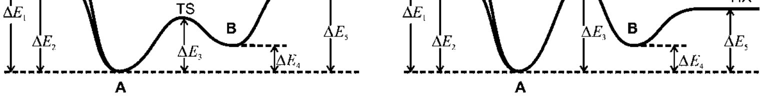

Figure 3. Possible free-energy profiles for the competing losses of methanol, HX, and X (X = F, Cl, Br) from cationic $X_2Fe(CH_3OH)^+$ complexes **A** as well as the isomeric $XFe(OCH_3)(HX)^+$ complexes **B** with the central transition structure lower [case a)] and higher in energy [case b)] than the lowest lying exit channels for ion dissociation. We note in passing that for X = Br the experimental data implies $\Delta E_1 < \Delta E_2$.

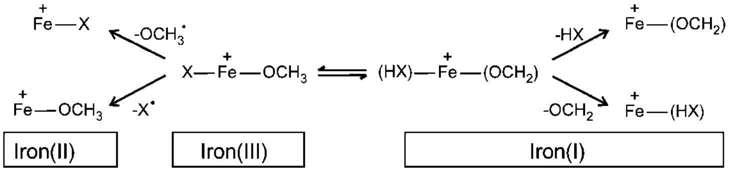

Figure 4. Redox tautomerization in the fragmentations of $XFe(OCH_3)^+$ (X = Cl, Br); loss of H_2CO is only observed for X = Br.

nated methanol molecules are observed in the spectra, thus suggesting that for X = Br, reaction (4) can already occur in solution.

The fragmentation patterns of the two unsolvated ions $ClFe(OCH_3)^+$ and $BrFe(OCH_3)^+$ reveals interesting redox properties of these species. In both cases, loss of hydrogen halide corresponds to the lowest-lying exit channel [*AE*(-HCl) = 0.5 eV; *AE*(-HBr) = 0.7 eV]. This requires a redox tautomerization in which CH_3O^- is oxidized to H_2CO and the electrons are formally transferred intramolecularly to the iron center, leading to an iron(I) complex $(HX)Fe(CH_2O)^+$ (X = Cl, Br) (Figure 4). The ability of methoxo ligands to transfer hydrogen atoms to the metal center via a ß-hydrogen shift has been long known[27,28] and it seems reasonable to assume that hydrogen is transferred to the halide ligand in a similar manner. Such rearrangements, in which an iron(III) species is reduced to iron(I) via a hydrogen transfer, have also been reported for the reaction of bare Fe^+ with dimethylperoxide.[29] Nevertheless, a direct tautomerization via a multicentered transition structure is also conceivable.[30]

For $BrFe(OCH_3)^+$, in line with the respective *AE*s, the loss of HBr prevails over the evaporation of CH_2O [*AE*($-CH_2O$) = 1.5 eV], which indicates a stronger binding of formaldehyde to the metal center than hydrogen bromide. In the case of X = Cl, the difference in bond strength is so distinct that the expulsion of H_2CO is not observed at all upon CID. The *AEs* corresponding to the respective direct homolytic bond cleavages show that breaking of the $ClFe^+$–(OCH_3) bond is easier [*AE*($-OCH_3$) = 2.4 eV] than breaking the Cl–$Fe(OCH_3)^+$ bond [*AE*(-Cl) = 3.5 eV]. In contrast, cleavage of the Br–$Fe(OCH_3)^+$ bond [*AE*(-Br) = 2.3 eV] is easier than breaking the $BrFe^+$–(OCH_3) bond [*AE*($-OCH_3$) = 2.8 eV]. Once solvent molecules are attached to these complexes, these mechanistically indicative evaporations of formaldehyde are not observed anymore, such that on the basis of the CID experiments, a further distinction of the structures of the parent ions is impossible. When two methanol molecules surround the ion core, i.e. for $XFe(OCH_3)(CH_3OH)_2^+$, the influence of the ligand again becomes most obvious: While the fluoride species loses HF besides methanol, evaporation of the solvent is the only fragmentation channel for $ClFe(OCH_3)(CH_3OH)_2^+$; for X = Br, also reductive cleavage of the iron-halide bond concomitant with the expulsion of atomic bromine from the precursor complex is observed.

Conclusions

The effects of the formal oxidation state, the nature of the halide, and the number of solvent molecules on the structures and energetics of iron-halide complexes are studied by electrospray mass spectrometry of methanolic FeX_m solutions (X = F, Cl, Br, I; *m* = 2, 3). The most abundant ions formed can be described as consisting of covalently bound FeX^+, FeX_2^+, and $XFe(OCH_3)^+$ cores, respectively, which are stabilized by various amounts of methanol molecules. For some halide ligands, solvolysis becomes energetically accessible upon collisional excitation once the effects of solvation are less dominant. This effect is particularly pronounced for all species containing fluorine as formation of HF via an intracomplex hydrogen transfer from a methanol molecule provides a strong thermodynamic driving force. The presence of methoxo ligands in turn facilitates the occurrence of C–H bond activation reactions via hydrogen migration leading to iron(I) compounds. In contrast, $Br_2Fe(CH_3OH)_n^+$-ions do not at all undergo intramolecular hydrogen transfer processes, and a pronounced tendency to undergo reductive loss of atomic bromine prevails instead. In comparison of the iron(II)- and iron(III) compounds, in line with general expectations solvation strongly stabilizes the iron(III) state. With decreasing solvation of the iron(III) species, the binding energies of the methanol accordingly enlarge and likewise the probability of the occurrence of redox reactions leading to either iron(II) or even iron(I) compounds increases.

Experimental Section

The mass spectrometric experiments were carried out with a commercial VG BIO-Q mass spectrometer described elsewhere.[31] In brief, the VG BIO-Q consists of an ESI source combined with a tandem mass spectrometer of QHQ configuration (Q: quadrupole, H: hexapole). In the present experiments, mmolar solutions of anhydrous FeX_2 (X = F, Cl, Br, I) and FeX_3 (X = F, Cl, Br) in methanol were introduced through a syringe pump (flow rate 5 µL/min) to the fused silica capillary of the ESI source. The source temperature was kept at 80 °C. For each ion of interest, the instrument parameters were optimized for maximal ion abundance. The most crucial parameter is the cone voltage U_C which determines the extent of collisional activation of the ions evolving from solution in the differential pumping system of the ESI source. At low cone voltages, multiply solvated ions are formed, which then lose the weakly bound solvent molecules at increased U_C, followed by evaporation of more strongly bound ligands including the cleavage of covalent bonds, electron-transfer processes, and atomic metal cations are obtained at very high cone voltages.

Collision-induced dissociation experiments were performed with Q1-selected ions and xenon was admitted as a collision gas to the hexapole at various collision energies (E_{lab} = 0–40 eV) and a pressure of about $2.5 \cdot 10^{-4}$ mbar, which approximately corresponds to single collision conditions.[31] The product ions formed in the hexa-

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pole were then analyzed by scanning Q2. The collision energies were converted into the center-of-mass frame, $E_{CM} = [m/(M + m)]\cdot E_{lab}$, in which M and m are the masses of the collision gas and the ionic species, respectively. Variation of the collision energy led to breakdown diagrams that enabled the determination of phenomenological appearance energies (*AEs*)[32] of the various fragmentation channels by linear extrapolation of the signal onsets to the baseline. The corresponding experimental errors were estimated by applying linear extrapolations with gradients deviating from the best possible fits, but which are still in reasonable agreement with the experimental data. It is to be pointed out that the *AEs* given below do not directly correspond to thermochemical thresholds of the respective ion dissociations, but nevertheless provide a frame for the energy demands of the various fragmentations.

Appendix. Thermochemical Estimates

In order to evaluate the stability of the two tautomers $FFe(CH_3OH)^+$ and $(HF)Fe(OCH_3)^+$, their heats of formation are estimated using Equation (5) and (6).[33]

$$\begin{aligned}&\Delta_f H(FFe(CH_3OH)^+) = \\ &\Delta_f H(FeF^+) + \Delta_f H(CH_3OH) - BDE(FFe^+ - (CH_3OH))\end{aligned} \tag{5}$$

$$\begin{aligned}&\Delta_f H((HF)Fe(OCH_3)^+) = \\ &\Delta_f H(Fe(OCH_3)^+) + \Delta_f H(HF) - BDE((OCH_3)Fe^+ - (HF))\end{aligned} \tag{6}$$

The exact values for the binding energies are unknown and have to be estimated using existing data. The binding energy of methanol to FeF^+ must be within the window of the binding energies of methanol to bare Fe^+ and to the iron(II)-chloride cation. Both these values can be found in the literature[15,34] (Table 4), and the binding energy to FeF^+ is estimated to correspond to their average [Equation (7)]. Note the excellent agreement with the *AE* for the loss of methanol from FeF^+ in Table 1.

$$\begin{aligned}&BDE(FFe^+ - (CH_3OH)) \approx \\ &\tfrac{1}{2}\left[BDE(Fe^+ - (CH_3OH)) + BDE((Cl)_2Fe^+ - (CH_3OH)\right] = (1.6 \pm 0.3) eV\end{aligned} \tag{7}$$

Table 4. Literature thermochemistry used.

	$\Delta_f H$ [eV]	Ref.		*BDE* [eV]	Ref.
FeF^+	8.0 ± 0.2	[33]	Fe^+–CH_3OH	1.39 ± 0.09	[34]
$FeOCH_3^+$	8.76 ± 0.08	[28]	$FeCl_2^+$–CH_3OH	1.79	[15]
CH_3OH	–1.94 ± 0.02	[39]	Cu^+–HF	0.76	[35]
HF	–2.64 ± 0.01	[39]	Cu^+–H_2O	1.41	[35]
			Cu^+–NH_3	1.98	[35]
			Cr^+–HF	0.66	[36]
			Cr^+–H_2O	1.23	[36]
			Cr^+–NH_3	1.67	[36]
			Fe^+–H_2O	1.27 ± 0.05	[38]
			Fe^+–H_2O	1.72 ± 0.09	[37]

The binding energy of HF to $Fe(OCH_3)^+$ is even more difficult to evaluate. A first simplification is to neglect the methoxide ligand, thus estimating the binding energy of HF to bare Fe^+. Unfortunately, even this value is unknown, but values for binding energies of HF to Cu^+ and Cr^+ exist, as well as values for the binding energies of H_2O and NH_3 to Cu^+, Cr^+, and Fe^+.[35–38] On the basis of this data, a rough approximation according to Equation (8), (9), and (10) is possible.

$$BDE(Cu^+ - (HF)) = x_1 \cdot BDE(Cu^+ - (H_2O)) = x_2 \cdot BDE(Cu^+ - (NH_3)) \tag{8}$$

$$BDE(Cr^+ - (HF)) = x_2 \cdot BDE(Cr^+ - (H_2O)) = y_2 \cdot BDE(Cr^+ - (NH_3)) \tag{9}$$

$$BDE(Fe^+ - (HF)) \approx x_{1,2} \cdot BDE(Fe^+ - (H_2O)) \approx y_{1,2} \cdot BDE(Fe^+ - (NH_3)) \tag{10}$$

The resulting binding energies range from 0.66 to 0.69 eV. Obviously the binding energy of HF to the iron(II) species $Fe(OCH_3)^+$ is larger than the one estimated to Fe^+; however, this should be a somewhat reasonable value. Inserting all data, including the known values for the heats of formation of FeF^+,[28] $Fe(OCH_3)^+$,[33] methanol and HF,[39] the following results are obtained:

$\Delta_f H[FFe(CH_3OH)^+] = (4.5 \pm 0.5)$ eV

$\Delta_f H[(HF)Fe(OCH_3)^+] = (5.5 \pm 0.2)$ eV

As some of the approximations made in the estimation of these quantities are quite crude, we do not claim the exactness of the results; nevertheless these considerations can at least provide a guideline for the understanding of the experimentally observed trends among the different halogens. In the particular case discussed here, the energy difference of about 1 eV clearly implies the conclusion that the iron-fluoride complex $FFe(CH_3OH)^+$ is energetically more favorable than the iron-methoxo isomer (HF)-$Fe(OCH_3)^+$.

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