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Preliminary communication

Gas-phase Ligation of $Cr^+/Fe^+/Ni^+$ Ions with Iodine

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Abstract. The gas-phase reaction products of Cr^+, Fe^+ and Ni^+ ions produced by laser desorption ionization (LDI) of a stainless steel sample with iodine molecules in a Fourier transform ion cyclotron resonance mass spectrometer (FT ICR MS) uncover differences in the behavior of individual metal ions in the ligation process as well as in the reactions with ubiquitous water: Fe^+ being prone to ligation of two (but also to hydrolysis and disappearance), Ni^+ to ligation of three and Cr^+ preferring to ligate four iodine atoms. The surplus energy of metal ions produced in the excited states enables them to dissociate I_2 and exchange charge with the I_2 molecules and I atoms forming I_2^+ and I_3^+ ions.

Keywords: ligation reaction, charge exchange reaction, metal monocations, iodine

INTRODUCTION

Single shot laser desorption ionization (LDI) of a stainless steel sample in a Fourier transform ion cyclotron resonance mass spectrometer (FT ICR MS) produces a mixture of $Cr^+/Fe^+/Ni^+$ ions that can react with neutral I_2 molecules present within the instrument at room temperature. The reaction of metal ions with iodine molecules at their relatively high concentration in the chamber is practically instantaneous: even after the shortest possible delay times (100 μs) the metal ions are completely consumed. It must be emphasized that many of the metal ions are produced in the excited states which can deactivate in the gas phase only by collisions.[1,2] Their surplus energy enables them to dissociate I_2 and exchange charge with the I_2 molecules and I atoms which otherwise have higher IPs (9.4 and 10.5 eV, respectively) than Cr, Fe and Ni (6.77, 7.90, and 7.64 eV, respectively). However, on varying the delay time it is still possible to track the follow-up reactions of the positively charged species that occur either with the remaining I_2 or some other neutral reactant (*e.g.* H_2O, I-atoms). The results uncover surprising differences in the behavior of the Cr^+, Fe^+ and Ni^+ ions in the ligation process as well as in the reactions with neutrals. We were unable to find the description of such behavior and present here the obtained results as a preliminary (short) communication. An investigation of solvent and ligand effects on the structures of iron halide cations in the gas phase by ESI MS using collision experiments and thermodynamic considerations has appeared recently.[3]

EXPERIMENTAL

LDI MS experiments were performed with a Nd:YAG laser (Quanta Ray DCR-11, Spectra-Physics, Mountain View, CA, USA) and a 3 T Fourier transform ion cyclotron resonance mass spectrometer (FT/MS 2001 DD, Finnigan, Madison, WI, USA). Metal ions were generated by a single laser pulse at 1064 nm from a stainless steel target containing $^{52}Cr : {}^{56}Fe : {}^{58}Ni$ in the ratio 23 : 65 : 12 which was used repeatedly in our previous studies of metal ion ligation.[4–6] Small crystals of iodine in a vial were introduced into the MS chamber and allowed to sublime at the ambient temperature of the instrument. At these conditions all iodine in the gas phase is expected to consist of I_2 molecules. The metal ions were allowed to react with them using various time delays (100 μs, 100 ms and 1 s) between the laser pulse and the recording of the mass spectrum.

RESULTS AND DISCUSSION

We present here the reaction products in form of main isotope bar graphs derived from positive ion FT mass spectra at three delay times of 100 μs, 100 ms and 1 s after the LDI that formed the metal ions in Figure 1. a, b and c, respectively.

The immediate (100 μs) products are the FeI^+, FeI_2^+, FeI_3^+ and FeI_4^+ from Fe^+, the CrI_2^+, CrI_3^+ and CrI_4^+ from Cr^+ and the NiI_3^+ from Ni^+, as well as the I_2^+ and I_3^+ from I_2 (and I) by reactions and charge exchange

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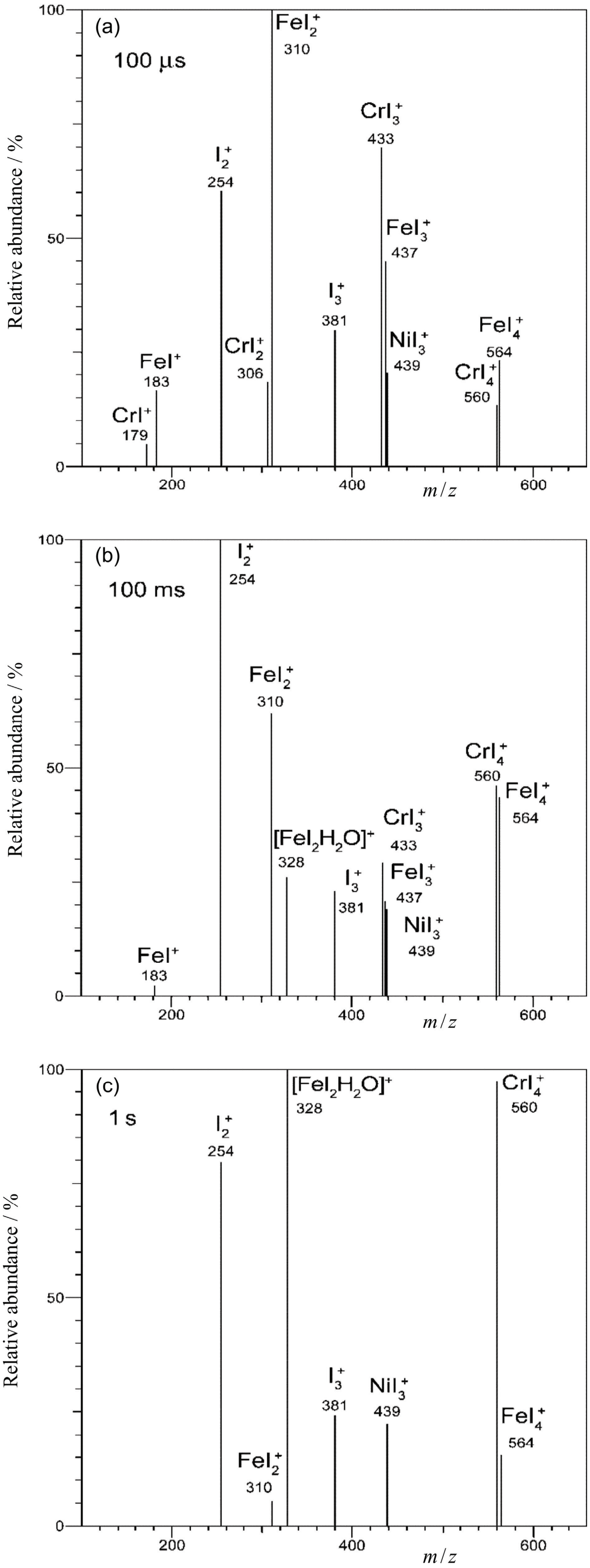

Figure 1. LDI spectra of the gas-phase reaction mixture of ^{52}Cr, ^{56}Fe and ^{58}Ni (23 : 65 : 12) with I$_2$ at different times after the laser pulse: 100 μs (a), 100 ms (b), 1 s (c).

with (excited) metal ions. The sums of intensities (in %) of metal-iodine products in ^{52}Cr : ^{56}Fe : ^{58}Ni = 34 : 59 : 7 correspond roughly to the fractions of ions the formed by LDI but those of Fe$^+$ and Ni$^+$ species being somewhat lower and of Cr$^+$ higher. The FeI_2^+ dominates the mass spectrum, followed by the CrI_3^+ species. Ni$^+$ does not show ligation products with 1, 2 and 4 iodine atoms.

After a 100 ms delay I_2^+ forms the base peak because nearly one third of FeI_2^+ reacts with the ubiquitous water in the instrument to form $(FeI_2H_2O)^+$. No such or similar reaction is seen in the spectra for any other species. Some Fe$^+$ still remains present but none of the Cr$^+$ and CrI_2^+ species. All the Cr$^+$ appears as CrI_3^+ and CrI_4^+ and all Ni$^+$ as NiI_3^+. The FeI_3^+ and FeI_4^+ are both lower in abundance than the corresponding CrI_3^+ and CrI_4^+ species. The ^{52}Cr : ^{56}Fe : ^{58}Ni fractions are in the ratio 32 : 63 : 5 at 100 ms.

After a 1 s delay time only a trace of FeI$^+$ and FeI_4^+ remains while $(FeI_2H_2O)^+$ forms the base peak. The only Ni$^+$ and Cr$^+$ species are NiI_3^+ and CrI_4^+ (nearly as high as $FeI_2H_2O^+$ base peak) The ^{52}Cr : ^{56}Fe : ^{58}Ni fractions are in the ratio 41 : 50 : 9 here.

Thus, the overall behavior that follows from Figures 1.a, b, c is Fe$^+$ being prone to ligation of two (but also to hydrolysis and disappearance), Ni $^+$ to ligation of three and Cr$^+$ preferring to ligate four iodine atoms. The fraction of combined I_2^+ and I_3^+ in the mass spectra increases from 22 to above 30 % which could be the result of charge loss and disappearance of Fe-iodine$^+$ species. We feel that such state of affairs deserves a better inspection.

To conclude, experiments on gas-phase ligation of monopositive metal ions with various ligands have revealed many surprising differences concerning both the type of metal and that of ligand.[7–9] Electronic structure of the metal ions and ligands, energy and steric (spatial) requirements influence and determine the different behavior resulting in different numbers and types of ligand binding (sandwich-, double- or single-bond). Such reasons are also operative in the present case which we intend to study in greater detail.

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SAŽETAK

Ligacija iona Cr$^+$/Fe$^+$/Ni$^+$ s jodom u plinskoj fazi

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Produkti reakcija Cr$^+$, Fe$^+$ i Ni$^+$, nastalih udarom lasera na čeličnu metu (LDI) unutar spektrometra masa ionsko ciklotronske rezonancije uz Fourierovu transformaciju (FT ICR MS), s molekulama joda u plinskoj fazi pokazuju različito ponašanje pojedinih metalnih iona u procesima ligacije kao i u reakciji s prisutnim tragovima vode. Tako je Fe$^+$ sklon ligaciji dva (uz hidrolizu i nestajanje), Ni$^+$ tri, a Cr$^+$ četri atoma joda. Višak energije iona metala u pobuđenim stanjima omogućava disocijaciju I_2 i reakcije izmjene naboja s molekulama i atomima joda uz nastajanje I_2^+ and I_3^+.