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Influence of the Ligand on the Gas-Phase Reactivity of Iron Complexes $Fe(CX)^+$ ($X = O, N, S, F_2, Cl_2$)

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Abstract : Ion-molecule reactivities of different one-carbon ligand complexes $Fe(CX)^+$ with oxygen and allyl chloride appeared strongly dependent on the nature and binding energy of the ligand. With oxygen ligand oxidation occurred for X = O, S. With allyl chloride coupling products were observed in the only case of the $Fe(CS)^+$ complex. © 1997 Published by Elsevier Science Ltd.

The reactivity of naked metallic cations has been largely studied[1] providing a large variety of new mono- or poly-ligated organometallic complexes. On the contrary, the reactivity of ligated species has been investigated more recently[2] and few works described the role and the influence of the ligands.[3] The study of ion-molecule reactions appeared as a useful tool to explore this new field. The corresponding information can be used in two ways : identifying the structure of ion precursors, and understanding the influence of the nature of the ligands on the preferred reaction pathways.

In the course of our work dealing with metal cations and complexes in ion-atom[4] or ion-molecule[5] reactions, we were very interested in characterizing different $Fe(CX)^+$ complexes ($X = O, S, N, Cl_2, F_2$) through their reactivity with oxygen and allyl chloride. Distinct behaviors were expected from these reactions; indeed, allyl chloride had been observed to give different types of coupling reactions with polyligated complexes $Fe(CO)_n^+$ [6] and $Fe(CN)(ICN)_n^+$ [7] whereas oxygen was known to give oxidation products and/or ligand exchange reactions.[8]

Two configurations have been sucessively used in our multiquadripolar MS/MS/MS instrument[9] for this series of experiments. Through the first configuration,[10] the determination of the reaction channel for the formation of the parent complex was effected in the first collision cell, whereas the reactivity and the structure of this parent were investigated in the second collision cell. Then, in the second configuration,[11] a supplementary reaction stage was provided by means of performing the first reaction in the ion source. The structures of the ion products formed in the first collision cell from the reaction with oxygen or allyl chloride were characterized in the second collision cell with collisionnally activated dissociations. Under normal reaction conditions, the kinetic energy of the incoming ions followed a distribution centered around 1 eV and ca 1 eV wide in the laboratory frame,[12] therefore allowing a maximumreaction endothermicity of ca 50 kJ mol^{-1}.

The first set of experiments revealed that the complexes under interest were produced by direct reaction on the naked iron ions. In fact, $Fe(CX)^+$ ions were only minor products of these reactions except in the case of $Fe(CN)^+$, which has been discussed in a previous paper.[5] The $Fe(CX)^+$ complexes could not be generated from $Fe(CO)_n^+$ reactions which led predominantly to ligand exchange products, for example $Fe(CO)_m(ICN)^+$ with ICN or $Fe(CO)_m(CS_2)^+$ with CS_2.

CAD experiments were performed with both configurations on the precursor complexes $FeCO^+$, $Fe(CS)^+$, $Fe(CN)^+$. The acceleration energy necessary for obtaining fragmentation increased in the following order, suggesting the same qualitative trend for the bond energies : $FeCO^+ < Fe(CS)^+ < Fe(CN)^+$. The CAD spectra consisted mainly in Fe^+ ion, which was the exclusive fragment from $Fe(CN)^+$, thus giving little information about structure. However $FeCO^+$ gave also traces of FeC^+, in accordance with the $(Fe\text{-}C\text{-}O)^+$ structure indicated by theoretical studies[13]. Similarly, $Fe(CS)^+$ gave a weak FeS^+ fragment, suggesting the presence of a $(Fe\text{-}S\text{-}C)^+$ structure. Ions $FeCF_2^+$ and $FeCCl_2^+$ could not be cleaved due to their very small intensity.[14]

Reactivity with oxygen was studied in order to gather further data concerning the structure of these $Fe(CX)^+$ complexes. This reagent gas has indeed allowed to distinguish $FeCNH^+$ and $FeNCH^+$ isomers producing specific daughter ions.[15]

A very small cross section had been determined for the reaction between bare Fe^+ ions and oxygen[16] leading to the single product FeO^+. In the presence of a CO ligand new pathways were detected (scheme 1).

scheme 1

$$\begin{array}{llll} Fe(CO)^+ + O_2 \rightarrow [Fe(CO)/O_2]^{+*} & \rightarrow FeO_2^+ + CO & (1) & 60\% \\ & \rightarrow FeO^+ + CO_2 & (2) & 17\% \\ & \rightarrow Fe^+ + (C,3O) & (3) & 23\% \end{array}$$

Channel (1), corresponding to ligand exchange, is endothermic by ca 25 kJ mol^{-1} [17]. Channel (2) is exothermic by 243 kJ mol^{-1}. Formation of CO_2 as neutral product is the most likely since formation of FeO^+ from $FeCO^+ + O_2$ has been observed to occur under thermalized conditions,[18] and the other possible reactions yielding FeO^+ are very endothermic. In the case of channel (3) the neutral products may be either $CO + O_2$, stemming from simple collisionally activated fragmentation, or $CO_2 + O$. These reactions are endothermic by 131 and 97 kJ mol^{-1} respectively; these values, especially the former one, are higher than the maximum endothermicity allowed under our conditions, but source ions $FeCO^+$ may be electronically excited. Therefore channel (1) and maybe channel (3) correspond to Fe^+-induced oxidation of CO.

The reactive pathways for $Fe(CS)^+$ are described in scheme 2.

scheme 2

$$\begin{array}{llll} Fe(CS)^+ + O_2 \rightarrow [FeCSO_2]^{+*} & \rightarrow FeO^+ + (C,S,O) & (1) & 60\% \\ & \rightarrow Fe^+ + (C, 2O, S) & (2) & 30\% \\ & \begin{array}{l} \rightarrow FeS^+ + CO_2 \\ \rightarrow FeO_2^+ + CS \end{array} & \left.\begin{array}{l} (3) \\ (4) \end{array}\right\} & 10\% \end{array}$$

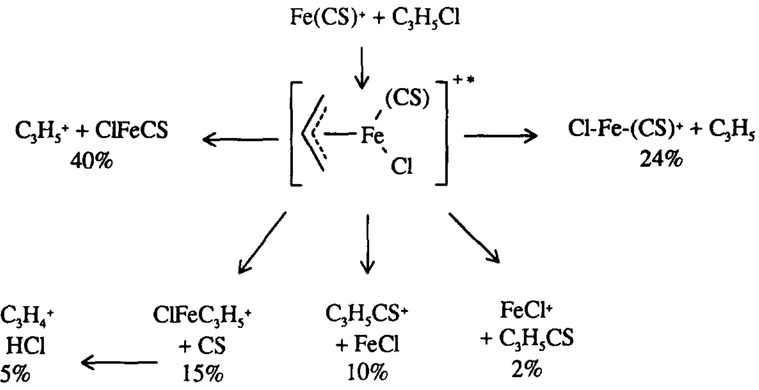
Channels (3) and (4), leading to isobaric ions (m/z = 102) FeS^+ and FeO_2^+, were differentiated by selecting $Fe(C^{34}S)^+$ isotopic parents with the first quadrupole; both $Fe^{34}S^+$ (m/z = 104) and FeO_2^+ (m/z 102) were detected in roughly similar amounts. The low amount of ligand exchange compared to $FeCO^+$ is consistent with the bond energy higher for CS than for CO. Formation of FeS^+ through channel (3) is another indication for Fe-S-C structure, but it is not conclusive since the reaction involves rearrangements. Channel (1) may involve formation of either CO + S or SCO, both exothermic (formation of CS + O would be too endothermic). Formation of a SCO molecule seems more likely by analogy with $FeCO^+$ reactivity. Concerning channel (2), simple fragmentation to $CS + O_2$ neutrals seems extremely unlikely since CAD experiments show that acceleration of $Fe(CS)^+$ ions is required to obtain a sizeable fragmentation extent. Other possible neutral products, in order of decreasing exothermicities, are CO_2 + S, CO + SO, and COS + O, all of which involving oxidation of the CS ligand.

No reaction was observed between oxygen and $Fe(CN)^+$ or $FeCF_2^+$ ions; $FeCCl_2^+$ ions only gave trace amounts of $FeCl^+$ and $FeCCl^+$. The ligand exchange was unlikely to happen because of the very strong binding energy, however oxygen-containing complexescould have been expected in analogy with $FeCS^+$ reactivity.

The reactivities of allyl chloride with Fe^+ and $FeCO^+$ have been reported :[6] whereas Fe^+ gives mainly $C_3H_5^+$ (which reacts further with allyl chloride), $FeCO^+$ also allows insertion of allyl chloride giving $Cl\text{-}Fe\text{-}(C_3H_5)^+$, along with $C_6H_{10}^{+\cdot}$ resulting from Fe^+-mediated coupling reaction. This is another example of the spectator behavior of CO ligandwhose presence is necessary to remove the excess of reaction energy.

Results with $Fe(CS)^+$ differedfrom $FeCO^+$ and reaction pathways are presented in scheme 3.

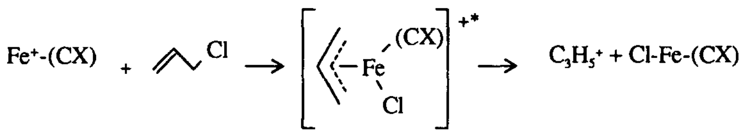
scheme 3



All the reaction products can be explained by the formation of an intermediate complex resulting from allyl chloride insertion, which fragments with or without rearrangement. C_3H_5 loss, still predominant, gave $C_3H_5^+$ and $Cl\text{-}Fe\text{-}(CS)^+$ ions. CAD spectrum of the latter product showed a single fragment $FeCl^+$, indicating a lower bond energy Fe^+-SC compared to Fe^+-Cl, i. e. $D_0(Fe^+\text{-}(CS)) < 330$ kJ mol^{-1}. Another reaction channel consists in the cleavage of Fe-(CS) bond (15%) which formally corresponds to a ligand exchange reaction. The last channel giving $C_3H_5CS^+$ and $FeCl^+$ ions, demonstrates the occurrence of a coupling reaction between CS and C_3H_5 ligands.

The reactivity of other complexes $Fe(CN)^+$, $FeCF_2^+$ and $FeCCl_2^+$ with allyl chloride were quite similar to bare Fe^+ reactivity, $C_3H_5^+$ ion, along with its further reaction products, was exclusively detected. Reaction of allyl chloride forms a intermediate complex (scheme 4) which stabilizes through loss of $C_3H_5^+$. The loss of $C_3H_5^\cdot$, which was observed as a minor reaction channel in the case of Fe^+ (leading to $FeCl^+$) and $Fe(CS)^+$ (leading to $Cl\text{-}Fe\text{-}(CS)^+$), does not occur here, since no Cl-Fe $(CX)^+$ was detected.

scheme 4



This study pointed out that reactions of metal complexes are highly dependent on the nature and bond strength of the (CX) ligands. While strongly bound CN, CF_2, CCl_2 ligands seem to have little effect on Fe^+ cation reactivity, the weakly bound CO ligand preferentially behaves as leaving group, whereas the CS ligand, possibly due to its intermediate binding energy, appears to be the most susceptible of Fe^+-mediated activation either by oxidation or by coupling with an allyl group. This study also raised the problem of the coordination Fe-C or Fe-X for these small ligands,particularly CN and CS;this question is still under investigation.

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10. (i) Ion source : $Fe(CO)_5$, (ii) first analyser Q1 : $Fe(CO)_n^+$ selection, (iii) first collision cell Q2 : reaction with ICN, CS_2, CF_3Br or CCl_3Br, (iv) second analyser Q3 : $Fe(CX)^+$ selection, (v) second collision cell Q4: CAD or reaction with O_2 or C_3H_5Cl, (vi) third analyser Q5 : scanning.
11. (i) Ion source : $Fe(CO)_5$ and ICN, CS_2, CF_3Br or CCl_3Br, (ii) Q1 : $Fe(CX)^+$ selection, (iii) Q2 : reaction with O_2 or C_3H_5Cl, (iv) Q3 : product ion selection, (v) Q4 : CAD, (vi) Q5 : scanning.
12 The decelerating potential V applied to the collision cell was normally adjusted to its maximum value allowing satisfying ion recovery. In order to estimate the kinetic energy distribution of the reactant ions, V was progressively increased starting from this value and the resulting ion intensity decrease was followed; the energy distribution was obtained by derivation.
13. (a) Barnes, L. A.; Rosi, M.; Bauschlicher, C. W. Jr. *J. Chem. Phys.* **1990**, *93*, 609-624. (b) Berthier, G.; Cimiraglia, R.; Daoudi, A.; Mestdagh, H. Rolando, C. Suard, M. *J. Mol. Struct. (Theochem)* **1992**, *254*, 43-49.
14. Under the CAD conditions allowing cleavage of $Fe(CS)^+$ (accelerating voltage 5-10 V), only the parent ion was detected. The very small intensity of the parent ions made impossible an increase of the accelerating voltage, since this increase normally results in an important signalloss.
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