Ligand Effects in σ-Bond Activation by Transition Metal-Ligand Complexes

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Abstract: Guided ion beam mass spectrometry has been used to examine the kinetic energy dependence of reactions of FeL^+ (L = CO and H_2O) with D_2. Activation of the D_2 bond by the ligated metal ions is observed. Thresholds for these processes are measured and converted to the following LFe^+-D bond dissociation energies (BDEs): $D_0(OCFe^+-D) = 1.35 \pm 0.08$ eV and $D_0(H_2OFe^+-D) = 2.26 \pm 0.12$ eV. Comparison of these values to the previously determined $D_0(Fe^+-D) = 2.16 \pm 0.06$ eV permits a quantitative assessment of the effects of ligation on σ-bond activation by metal complexes. Differences in the abilities of the two FeL^+ species to activate D_2 and to bond to a deuterium atom are rationalized in terms of the electronic structure at the ligated metal ion center.

During the last 15 years, a tremendous amount of experimental work has focused on the ability of "naked" atomic metal ions to activate C–H and C–C bonds of saturated alkanes in the gas-phase.[1–4] Many fewer studies have examined how this reactivity changes as the metal center is systematically ligated. Some studies have demonstrated that the reactivity of a gas-phase atomic metal ion can be dramatically altered by the addition of a single ligand,[5–8] although many of these studies provide little quantitative information on these differences and most involve ligands (such as an oxo ligand) that participate directly in the reactions. In the present study, we examine how ligation (with species that are not actively involved in the chemistry) affects the simplest case of σ-bond activation, the activation of dihydrogen. By using guided ion beam methods, we are able to quantitatively assess both the kinetic and the thermodynamic differences in the reactions. Related studies that demonstrate that σ-bond activation is enhanced for multiply ligated metal ions have recently appeared,[9] but, in this work, the ligands and the activated molecules are the same, thereby restricting the ability to "tune" the metal reactivity.

Our initial studies of such ligation effects center on the activation of D_2 (used instead of H_2 to enhance mass resolution) at an ionic iron center. Iron is chosen because we have previously[10] characterized the state-specific chemistry of this reaction with Fe^+ in its ground $^6D(4s^13d^6)$ electronic state and its $^4F(3d^7)$ first excited state, 0.23 eV higher in energy.[11] The excited state was found to be about 80 times more reactive than the ground state at threshold. The ligands chosen for investigation here include CO and H_2O, chosen because we have previously determined the thermodynamic properties of their iron cation complexes,[12,13] and the electronic properties of these complexes have been theoretically characterized.[14,15] Our collision-induced dissociation (CID) studies have determined that the bond dissociation energies (BDEs) relative to the $Fe^+(^6D)$ asymptote for the two complexes are essentially equal: $D_0(Fe^+-CO) = 1.36 \pm 0.08$ eV[12] and $D_0(Fe^+-H_2O) = 1.32 \pm 0.05$ eV.[13] Theory finds that the ground state of $FeCO^+$ is $^4\Sigma^-$,[14] while that of FeH_2O^+ is $^6A_1$,[15] and both interactions have been calculated to be largely electrostatic in nature. Thus, the reactivities of these two complexes are expected to be different based on electronic but not on thermodynamic considerations.

The guided ion beam apparatus used in these studies and our data reduction procedures have been described previously.[16,17] FeL^+ (L = H_2O and CO) ions are produced in a meter-long flow tube ion source[16] as described in detail elsewhere.[12,13] The ions undergo $\sim10^5$ collisions with the buffer gas before exiting the flow tube, and therefore are expected to have equilibrated to a temperature of 300 K with respect to all internal states. Previous work on a number of systems[12,18–20] is consistent with the production of thermalized ions under similar conditions. The FeL^+ ions are mass and energy selected and then interact with D_2 under single-collision conditions inside an octopole ion trap.[16,21] Reactant and product ions are mass analyzed and detected, and their intensities are converted to absolute cross sections.[16]

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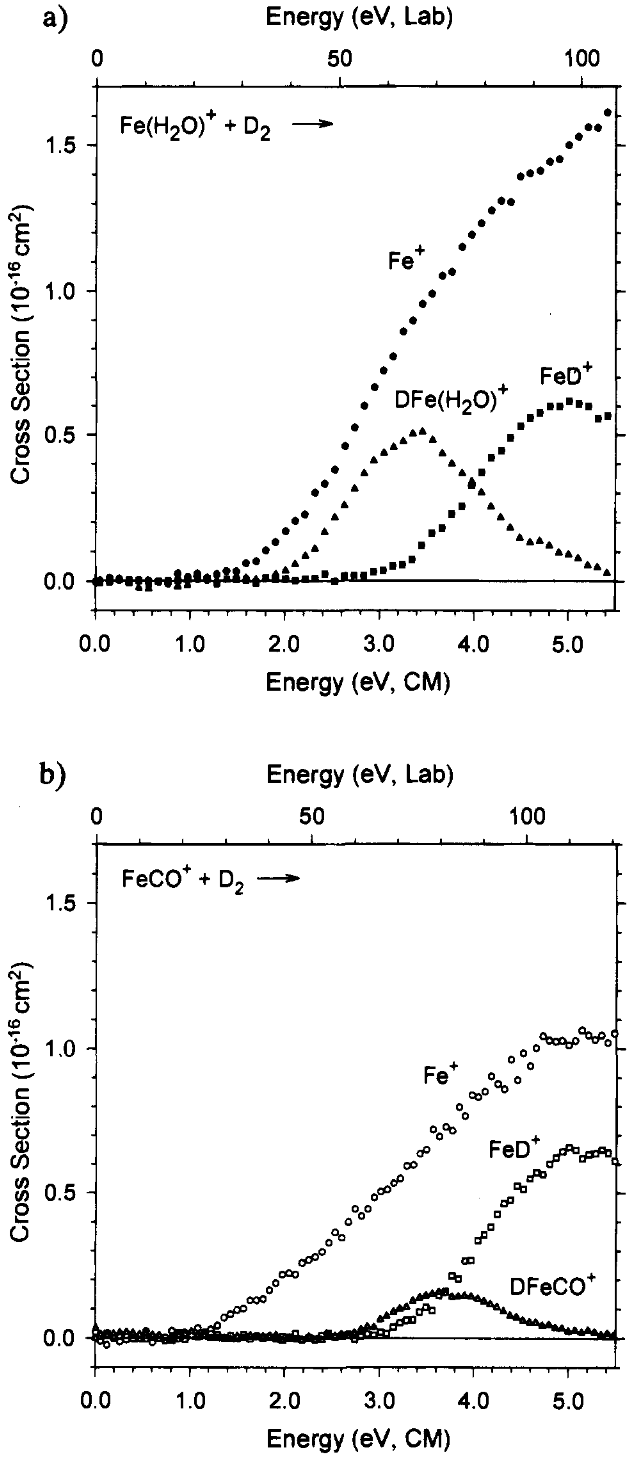

Figure 1. Cross sections for reaction of D_2 with FeL^+ (part a, L = H_2O; part b, L = CO) with D_2 as a function of relative kinetic energy (lower *x*-axis) and laboratory energy (upper *x*-axis).

Results for the interaction of D_2 with FeL^+ where L = H_2O and CO are shown in Figure 1. In both systems, we observe three products formed in reactions 1–3

$$\mathrm{FeL^+ + D_2 \rightarrow Fe^+ + L + D_2} + 1.32 \pm 0.05\ (1.36 \pm 0.08)\ \mathrm{eV} \quad (1)$$

$$\mathrm{\rightarrow DFeL^+ + D} \quad (2)$$

$$\mathrm{\rightarrow FeD^+ + L + D} + 3.72 \pm 0.08\ (3.76 \pm 0.10)\ \mathrm{eV} \quad (3)$$

where the known thermochemistry is indicated for L = H_2O (CO). The major product is Fe^+, formed in the simple CID reaction 1. This was confirmed by examining the reaction of FeL^+ with He and finding that the Fe^+ cross sections in the threshold regions are superimposable with those shown in Figure 1. As the energy is increased, the two channels involving D_2 activation, reactions 2 and 3, are observed. It can be seen that these channels are coupled because the cross section for the $DFeL^+$ product begins to decline at an energy where the ligand L can fall off, the threshold for formation of FeD^+.[22] It can be seen that the thresholds for reactions 1 and 3 are similar in the two systems (consistent with the similar Fe^+–L BDEs), but the thresholds for reaction 2 differ by almost an electron volt. This leads to a much larger cross section for $DFeH_2O^+$ compared to $DFeCO^+$, Figure 1.

Table 1. Thermodynamic Information

bond	bond energy (eV)	bond	bond energy (eV)
Fe^+–D	2.16 ± 0.06[a]		
H_2OFe^+–D	2.26 ± 0.12[b]	$OCFe^+$–D	1.35 ± 0.08[b]
Fe^+–H_2O	1.32 ± 0.05[c]	Fe^+–CO	1.36 ± 0.08[d]
DFe^+–H_2O	1.42 ± 0.14[b]	DFe^+–CO	0.55 ± 0.13[b]

[a] Reference 10. [b] This work. [c] Reference 13. [d] Reference 12.

Quantitative analysis of the energy dependence of these cross sections was achieved using methods that are outlined elsewhere.[12,13,23,24] As discussed elsewhere,[25,26] He and likewise D_2 are inefficient collision gases for inducing dissociation and therefore the cross sections for reaction 1 rise slowly from threshold. Nevertheless, the threshold regions of these cross sections can be modeled using the thermodynamic thresholds. It is interesting to note that this result (i.e., $FeCO^+$ dissociates in a spin-forbidden process to form $Fe^+(^6D)$ + CO) is different than the behavior observed when Xe is used as the collision gas, where spin-allowed dissociation to form $Fe^+(^4F)$ + CO is observed.[12] Further studies of this difference are being pursued.[27] This may explain why the magnitude of the Fe^+ cross section is somewhat higher for the FeH_2O^+ system, where the dissociation is spin-allowed. The cross sections for reactions 3 can also be modeled accurately using the thermodynamic thresholds listed above. In the case of reaction 2, our analysis yields thresholds for the formation of $DFeH_2O^+$ of 2.30 ± 0.12 eV and for $DFeCO^+$ of 3.21 ± 0.08 eV. These thresholds can be converted to the bond energies given in Table 1 if it is assumed that there are no activation barriers in excess of the endothermicities of reactions 2. This is often the case for ion–molecule reactions[24] and has been shown to be true for the unligated analogue of reaction 2.[10]

The results shown in Table 1 indicate that while the H_2O ligand slightly enhances the Fe^+–D BDE compared to the unligated metal ion, the CO ligand diminishes this BDE. Concomitantly, adding a deuterium atom to Fe^+ slightly enhances the metal–water binding and destabilizes the metal–CO interaction. This thermodynamic effect is consistent with the reactivity differences observed in reaction 2. Theoretical

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(22) It is possible that the deuterium atom in the $DFeL^+$ species is bound to the ligand (forming a formyl ligand when L = CO) rather than to the metal. However, the observation that both $DFeL^+$ species dissociate at the thermodynamic threshold into FeD^+ is suggestive of a $DFeL^+$ geometry. Although this does not definitively determine the ground state structures, any alternate structures must be able to rearrange to the $DFeL^+$ structure in order to eject L at higher energies.

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calculations of these species will be useful to characterize the details of their electronic structure, but we can understand these changes in bonding in the following qualitative fashion. The ground state of FeH_2O^+ is $^6A_1$ with an Fe^+ occupation of $4s^1 3d\sigma^1 3d\pi^2 3d\delta^3$ derived from the $^6D(4s^1 3d^6)$ ground state of Fe^+.[15] In order to reduce the repulsion between the occupied 4*s* orbital and the electron donating water ligand, the 4*s* orbital mixes in 4*p* character to polarize away from the ligand.[15] It is known that the first row transition metal ions use the 4*s* orbital to bind hydrogen atoms,[28-30] such that a deuterium atom can make a strong bond with this FeH_2O^+ configuration.

In contrast, the ground state of $FeCO^+$ is $^4\Sigma^-$ with an Fe^+ occupation of $3d\sigma^1 3d\pi^4 3d\delta^2$ derived from the $^4F(3d^7)$ state of Fe^+, and there is some 4*s*-3*dσ* hybridization.[14] In essence, the CO ligand locks the Fe^+ into this $3d^7$ configuration, and therefore $FeCO^+$ does not have an unpaired 4*s* electron to make a strong bond with a D atom. Formation of $DFeCO^+$ presumably involves binding D to the 3*dσ* molecular orbital (resulting in a weaker bond than for a 4*s*-1*s* bond) or $FeCO^+$ must promote an electron to a 4*s* orbital which costs energy and weakens the Fe^+−CO interaction. (Indeed, the DFe^+−CO BDE is comparable to the binding energy for CO to the ^6D state of Fe^+.[14])

The relative abilities of $FeCO^+$ and FeH_2O^+ to activate D_2 observed here are somewhat surprising if one imagines that the $FeCO^+(^4\Sigma^-)$ should react similarly to the more reactive $Fe^+(^4F)$ and that $FeH_2O^+(^6A_1)$ should react similarly to the less reactive $Fe^+(^6D)$. Instead, the magnitude of the cross section for formation of $DFeH_2O^+$ is larger than for $DFeCO^+$ and both are between those observed for production of FeD^+ in the reaction of the two atomic states of Fe^+ with D_2.[10] As discussed elsewhere,[4,10] D_2 activation at a metal center can be thought of as a process in which the D_2 σ-bonding orbital donates electron density into an acceptor orbital on the metal and the metal back donates π-electron density into the antibonding D_2 orbital. For first row atomic transition metal ions, the acceptor orbital is the 4*s* and the donor is the 3*dπ*. Thus, $Fe^+(^4F,3d^7)$ is more reactive than $Fe^+(^6D,4s^1 3d^6)$ because the acceptor orbital is empty in the former state and occupied in the latter. For the ligated Fe^+ ions, the π-back donation necessary to activate D_2 should be enhanced by the π-donating H_2O ligand[31] and suppressed by the π-accepting CO ligand. Differences in the characteristics of the acceptor orbitals in the ligated species are harder to ascertain because CO and H_2O are both σ-donating ligands. It seems likely that the acceptor orbital in $FeCO^+$ is the singly occupied 3*dσ* molecular orbital because the other 4*s*-like molecular orbital is already accepting two electrons from the CO ligand (and it is unfavorable to donate the D_2 electrons into the antibonding Fe−CO orbital). In FeH_2O^+, the likely acceptor is the singly occupied 4*s*-like molecular orbital polarized away from the ligand.[32] Thus, FeL^+ is less reactive than $Fe^+(^4F)$ because the acceptor orbitals are singly occupied in the ligated species rather than empty.

Preliminary investigations in our laboratory indicate that the reactivity differences between FeH_2O^+ and $FeCO^+$ observed here are also evident in the C−H and C−C bond activation of more complex hydrocarbon systems. The prospects that other reactions can be selectively "tuned" by systematic variations in electronic structure at the metal induced by ligation is a fascinating one.

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[32] A referee points out that a complication in this system is that there is a low-lying $^4A_1$ excited state of FeH_2O^+, ref 15, that probably binds D_2 more strongly than the $^6A_1$ ground state. Thus, there is the possibility of a curve crossing between sextet and quartet surfaces when $FeH_2O^+(^6A_1)$ interacts with D_2. This may actually provide a mechanism for avoiding the repulsion between the 4s-like MO on $FeH_2O^+(^6A_1)$ and D_2.