Dramatic Ligand Effects on Gas-Phase Transition-Metal Reactivity and Selectivity: Studies of Fe^+, $Fe^+(H_2O)$, and $Fe^+(CO)$ with Propane

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Received August 14, 1997⊗

Summary: The kinetic energy dependent reactions of ligated iron ions (FeL^+) with propane are examined using a guided ion beam mass spectrometer. In analogy with previous observations for atomic iron ions, propane reacts with both $Fe^+(H_2O)$ and $Fe^+(CO)$ by dehydrogenation to form $LFe^+(C_3H_6)$ and by demethanation to form $LFe^+(C_2H_4)$ in exothermic processes. These processes are barrierless in all cases except demethanation by $Fe^+(CO)$. Dramatic changes in the overall reactivity and selectivity are observed upon ligation. $Fe^+(H_2O)$ has a reactivity at thermal energies comparable to that of $Fe^+(^6D)$ and about two orders of magnitude larger than that of $Fe^+(CO)$. Atomic iron ions form $Fe^+(C_2H_4)$ three times more efficiently than $Fe^+(C_3H_6)$, while demethanation is favored by a factor of about 25 for reaction of $Fe^+(H_2O)$, and for $Fe^+(CO)$ dehydrogenation is preferred by over an order of magnitude. Although a definitive explanation of these interesting results is not yet available, several factors that play influential roles are discussed.

Introduction

One of the ultimate goals of homogeneous catalysis is to "engineer" species that will catalyze a desired process with efficiency and specificity. The prospects of an intelligent engineering process rely on understanding how the environment surrounding the active site in the catalyst influences its reactivity. Adjustments of the electronic structure of the site and its kinetic behavior are both clearly important. We[1−4] and others[5] have long been fascinated by the observation that atomic gas-phase transition-metal ions efficiently activate both C−H and C−C bonds in alkanes. In parallel with this work, we have begun systematic investigations of how ligation affects the electronic structure at the transition-metal center.[6] By merging these two related research activities, we and others[7] hope to elucidate how ligation can influence the reactivity at the transition-metal center in ways that can be understood quantitatively. In previous work, we have examined the reactions of Fe^+ ligated by CO and H_2O with D_2,[8] CH_4, and C_2H_6.[9] Here, we extend these studies to examination of the reactions of $Fe^+(CO)$ and $Fe^+(H_2O)$ with propane, the smallest alkane that reacts with atomic Fe^+ by exothermic pathways. In this preliminary report, we concentrate on the dramatic changes in these exothermic pathways induced by ligation. Forthcoming is a more complete analysis of all reaction pathways, including deuterium labeling studies and many endothermic processes that parallel our previous observations with the smaller alkanes.[10]

Experimental Section

The present studies are conducted using a guided ion beam mass spectrometer described in detail previously.[11] The iron ion complexes are formed in a 1 m long flow tube ion source[12] which uses a dc discharge to generate Fe^+. The ligand of choice is introduced downstream and formed by three body collisions. Further collisions with the flow gases (90% He and 10% Ar) thermalize these complexes. The desired ion is focused through a magnetic sector for initial mass analysis and then injected into a rf octopole beam guide[13] that passes through a cell filled with propane at pressures sufficiently low that multiple ion−molecule collisions are improbable. The kinetic energy of the ion beam is adjusted by setting the potential difference between the source and the guide. The advantages of using an octopole in the reaction region are well-documented. Reactant and product ions drift to the end of the octopole where they are extracted, mass analyzed with a quadrupole, and detected using a Daly detector and pulse-counting electronics. Ion intensities are converted to absolute reaction cross sections,[11] which are believed to be accurate to

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⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1997.

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S0276-7333(97)00718-8 CCC: $14.00

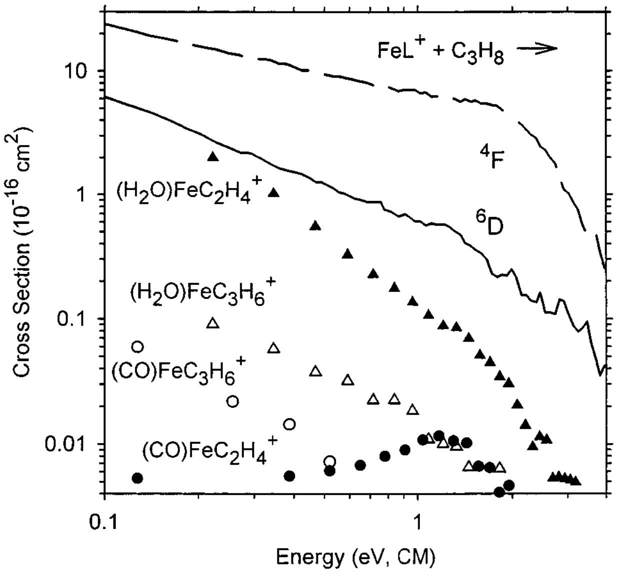

Figure 1. Cross sections for the exothermic reaction of ligated iron ions with C_3H_8 as a function of kinetic energy in the center of mass frame. Triangles and circles show the results for reaction of $Fe^+(H_2O)$ and $Fe^+(CO)$, respectively. Dehydrogenation and demethanation processes are shown by open and closed symbols, respectively. Total cross sections for reactions 1 and 2 with atomic iron ions in the ^6D and ^4F states are also shown by solid and dashed lines, respectively.

20%. The zero and distribution of the ion kinetic energy are determined using a retarding method in the octopole. Uncertainties in the energy scale are approximately 0.05 eV in the lab frame. Energies available for chemical change (center of mass frame) are determined using $E_{CM} = E_{lab}m/(M + m)$ where m and M are the masses of the neutral and ionic reagents, respectively.

Results and Discussion

Atomic transition metal ions react with propane in two exothermic pathways to yield ethene and propene bound to the metal ion, as shown for the case of iron (L not present) in reactions 1 and 2.[2,3] The results for these

$$Fe^+(L) + C_3H_8 \rightarrow LFe(C_2H_4)^+ + CH_4 \qquad (1)$$

$$\rightarrow LFe(C_3H_6)^+ + H_2 \qquad (2)$$

reactions where L = H_2O and CO, shown in Figure 1, indicate that both complexes undergo reactions 1 and 2 to demethanate and dehydrogenate propane. Clearly, the total reactivity of $Fe^+(H_2O)$ is much higher than that of $Fe^+(CO)$, by about two orders of magnitude at low energies. Previous studies of these two ligated complexes with D_2, CH_4, and C_2H_6[8,9] also found that $Fe^+(H_2O)$ was the more reactive species, but the magnitude of the difference is much larger in the exothermic reactions of the propane system. It might be noted that the thermal reactivity of propane with atomic iron ions, which has been characterized in both the ^6D and ^4F electronic states,[2,3,14] is comparable to the cross section observed for $Fe^+(H_2O)$, Figure 1. The energy dependence of the cross section for the $Fe^+(H_2O)$ complex declines more rapidly with energy than that for $Fe^+(^6D)$, which in turn falls off faster than that for $Fe^+(^4F)$, which parallels the energy dependence of the ion−molecule collision cross section. These faster declines indicate energy dependent inefficiencies for reaction of $Fe^+(^6D)$, generally attributed to the coupling from sextet to quartet spin surfaces, and $Fe^+(H_2O)$, which must have a similar origin.

The most interesting observation in Figure 1 concerns the selectivity of the reaction, which is inverted for the two different ligand systems. For atomic iron ions, reaction 1 is preferred over reaction 2 by a factor of about 3, a ratio that is essentially independent of the energy and electronic state.[2] $Fe^+(H_2O)$ shows a similar preference for the demethanation reaction, but now the ratio is about a factor of 20−30 at low energies. In contrast, $Fe^+(CO)$ favors dehydrogenation by a factor of at least 10. Indeed, it appears as though the demethanation reaction with $Fe^+(CO)$ exhibits a barrier to reaction,[15] in contrast to the other processes shown. Estimates of the bond energies in the $Fe^+(CO)(C_2H_4)$ product suggest that this reaction is quite exothermic (see below), hence we conclude that there is a barrier along the reaction coordinate for this process that is higher than the energy of the reactants.

The most challenging aspect of this study is the understanding of why such large changes in reactivity and selectivity occur. It does not appear to be an effect determined by the overall thermodynamics of these reactions. The bond energies of $Fe^+(H_2O)$ and $Fe^+(CO)$ are very similar (128 ± 5[16] and 131 ± 8[17] kJ/mol, respectively) as are the second bond energies, $(H_2O)Fe^+{-}OH_2$ and $(CO)Fe^+{-}CO$ (164 ± 4[16] and 151 ± 5[17] kJ/mol, respectively), which should roughly reflect the stabilities of the products shown in Figure 1. The $Fe^+(C_2H_4)$ and $Fe^+(C_3H_6)$ bond energies are also similar (145 ± 6[18] and 145 ± 7[19] kJ/mol, respectively). However, there may be some interesting synergistic effects at work given that the alkenes and CO are π-acceptor ligands while H_2O is a weak π-donor. Hence, the stabilities of the $Fe^+(H_2O)$(alkene) products and related reaction intermediates probably exceed those of the $Fe^+(CO)$(alkene) products. The observation that the demethanation reaction exhibits a barrier that cannot be attributed to an overall endothermic reaction (this would require that $(CO)Fe^+{-}C_2H_4$ be less than 77 kJ/mol) is the clearest demonstration that the overall energetics are not limiting in these reactions.

Therefore, we look to more subtle electronic effects to explain our observations. Theoretical work on the $Fe^+(H_2O)$ and $Fe^+(CO)$ complexes finds that they have different ground state electronic configurations. Calculations indicate that the ground state of $Fe^+(CO)$ is $^4\Sigma^-$ with a $3d\sigma^1 3d\pi^4 3d\delta^2$ configuration,[20] while $Fe^+(H_2O)$ has a $^6A_1$ ground state with a $4s^1 3d\sigma^1 3d\pi^2 3d\delta^3$ config-

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uration[21] (although there is also a low-lying quartet excited state). Note the distinct difference in π orbital occupations that reflect the π-donating ability of water vs the π-accepting ability of CO. Naively, we might have expected that $Fe^+(H_2O)$ ($^6A_1$) would react similarly to $Fe^+(^6D)$ and that $Fe^+(CO)$ ($^4\Sigma^-$) would be comparable to $Fe^+(^4F)$. Indeed, the overall reactivities of $Fe^+(H_2O)$ and $Fe^+(^6D)$ are comparable, and both species favor the demethanation channel, however, there is an appreciable change in the branching ratio between dehydrogenation and demethanation: 1:3 for $Fe^+(^6D)$ vs 1:~25 for $Fe^+(H_2O)$. $Fe^+(^4F)$ and $Fe^+(CO)$ clearly have very different reactivities and selectivities for reaction.

The clearest distinction between the H_2O and CO ligands lies in the interaction with the π orbitals on the metal. Both experiment[22,23] and theory[24] have demonstrated that the activation of σ bonds at metal centers can be thought of as donation of the bonding electrons to an acceptor orbital on the metal and back-donation of π electrons on the metal into antibonding orbitals of the σ bond to be broken. Therefore, the efficiency for C−H and C−C bond activation should be enhanced by the presence of a π-donor ligand like H_2O and suppressed by a π-acceptor ligand like CO. The dramatic changes in the reactivities suggest either that the rate-limiting transition states (TSs) associated with dehydrogenation and demethanation are grossly affected by ligation (especially by CO) or that these TSs are already close in energy to the reactant asymptote, such that small changes can lead to large effects. The latter conclusion is plausible as there is previous evidence that the TSs in the atomic iron ion reactions do lie close in energy to the reactants.[3] The present results also suggest that the rate-limiting TSs for dehydrogenation and demethanation are distinct from one another (in contrast to previous suggestions),[3] otherwise the changes induced by ligation should be the same for both channels. Of course, the present results only demonstrate this for the ligated species (definitively so for $Fe^+(CO)$), but this conclusion seems likely to hold for the bare metal ion as well. This observation is consistent with recent experiment[25] and theory[26,27] on the mechanism for reactions of atomic metal ions with alkanes.

It is also conceivable that the CO ligand suppresses the reactivity because it becomes intrinsically involved in the chemistry by C−C bond coupling reactions (i.e., formation of ketones, acetyl groups, etc.). More complete analysis of the $Fe^+(CO)$ system provides some indication that such coupling is occurring, although the extent of these processes appears to be small.

Acknowledgment. This work is supported by the National Science Foundation (Grant No. 9530412).

OM970718W

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