Alder reaction by I_2 is consistent with our original hypothesis that **1**·FeX_2^+ should be the catalytic species since I_2 is expected to favor cation generation by the process **1**·FeI_3 + I_2 → **1**·FeI_2^+ + I_3^-, because of the affinity of I_2 for I^-.[12]

The chiral ligand **1** is readily and efficiently recoverable from these catalytic Diels–Alder reactions for reuse. Because of this fact, the ready availability of ligand **1**, and the low cost of iron salts, the methodology described herein promises to be practical.

The structural rigidity of the **1**·FeX_2^+ system permits a rational analysis of the stereochemical results described above, assuming that the C=C/C=O s-cis form of dienophile **4** chelates to **1**·FeX_2^+ prior to reaction with cyclopentadiene. If dienophile **4** chelates to **1**·FeX_2^+ via the equatorial sites e_1 and e_2 in **6**, the product of the Diels–Alder reaction clearly should be the 2*S* adduct rather than the 2*R* adduct **5** which is observed. This must not be the major binding mode for the catalytic pathway, and therefore, chelation to **1**·FeX_2^+ via a and e sites in **6** is indicated. Since site a_2–e_1 (or the C_2 equivalent a_1–e_2) is sterically unfavorable relative to a_1–e_1 (or its C_2 equivalent), the a_1–e_1 site should be preferred. Although there are two possible chelates of dienophile **4** at the a_1–e_1 site, the favored pathway for each chelate is that leading to 2*R*-adduct **5**, as observed experimentally.

The conclusion that the chelation of dienophile **4** with **1**·FeX_2^+ occurs at an a–e site rather than at the e–e site raises the question of why coordination of **4** at the e–e site is kinetically less favorable. One interesting possibility emerges from the likelihood that complex **1**·FeX_2^+ possesses square-planar geometry and that chelation of dienophile **4** takes place by the sequence (1) coordination of one of the carbonyl oxygens of **4** to an axial site and (2) chelate ring closure with e → a transposition of X. This pathway clearly would lead to predominant formation of the a–e chelate of **4**, as required for the above described mechanistic model.

Further study is planned to optimize this new enantioselective Diels–Alder addition, to determine its scope, and to gain deeper insights as to mechanism.[13,14]

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(12) For examples of cationic complexes of aluminum with 3-acryloyl-1,3-oxazolidines as reactive species in Diels–Alder reactions, see: Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238–1256.

(13) The following procedure illustrates the catalytic Diels–Alder reaction with **1**·FeI_3 and I_2 to form adduct **5**. To a mixture of 15.2 mg (0.272 mmol, 0.10 equiv) of powdered iron and 104 mg (0.408 mmol, 0.15 equiv) of iodine was added 2 mL of anhydrous CH_3CN. After stirring for 1 h at 40 °C, a solution of 109 mg (0.326 mmol, 0.12 equiv) of the bis(oxazoline) **1** in 2 mL of anhydrous CH_3CN was added dropwise at 23 °C to the black solution. The solution was stirred for 1 h at 40 °C and evaporated to afford a dark viscous oil, which was dissolved in 7 mL of anhydrous CH_2Cl_2 and treated at −78 °C with 69.1 mg (0.272 mmol, 0.10 equiv) of iodine, 385 mg (2.73 mmol, 1 equiv) of 3-acryloyl-1,3-oxazolin-2-one (**4**),[9] and 0.68 mL (8.19 mmol, 3 equiv) of precooled cyclopentadiene. After stirring for 2 h at −50 °C, the dark brown solution was quenched with 0.1 mL of Et_3N, diluted with ether–pentane, and washed first with aqueous sodium sulfite and then with aqueous cupric acetate. The organic layer was dried and concentrated in vacuo, and the crude product was chromatographed on silica gel with a 1:1 mixture of ethyl acetate and hexane to afford 539 mg (95% yield, endo:exo = 96:4, 82.2% ee) of 1*R*,2*R*,4*R*-adduct **5**.[2c,9] The ee was determined by HPLC analysis using a Daicel OD column with 10% *i*-PrOH in hexane for elution (1 mL/min; retention times 23.5 min for **5** and 21.4 min for the enantiomer of **5**). Treatment of the aqueous $Cu(OAc)_2$ extract described above with NH_4OH and extraction with 4:1 ether–CH_2Cl_2 afforded ligand **1** (>85%) for reuse.

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Threshold Collisional Activation of $Fe^+\cdot C_3H_8$: Probing the Potential Energy Surface

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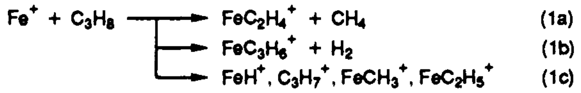
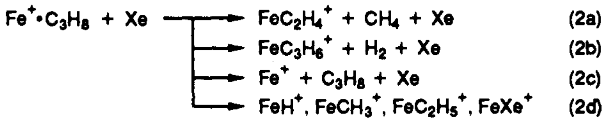
The bimolecular reaction of Fe^+ with propane has been the subject of considerable research during the past decade, spanning a wide variety of gas-phase experimental techniques.[1,2] Two exothermic processes are observed, reactions 1a and 1b, and several endothermic processes, reactions 1c. Since reactions 1a and 1b are barrierless, elucidating details of the potential energy surface (PES) of reaction 1 is difficult. Here, we describe a novel experiment that allows us to probe such details by entering the PES at a different place, namely, the bottom of the well associated with the assumed initial intermediate for reaction 1, the ion induced dipole bound complex, $Fe^+\cdot C_3H_8$.[2] We then collisionally activate this species to induce reactions 2a–d.



$$Fe^+ + C_3H_8 \rightarrow FeC_2H_4^+ + CH_4 \quad (1a)$$
$$\rightarrow FeC_3H_6^+ + H_2 \quad (1b)$$
$$\rightarrow FeH^+,\ C_3H_7^+,\ FeCH_3^+,\ FeC_2H_5^+ \quad (1c)$$



$$Fe^+\cdot C_3H_8 + Xe \rightarrow FeC_2H_4^+ + CH_4 + Xe \quad (2a)$$
$$\rightarrow FeC_3H_6^+ + H_2 + Xe \quad (2b)$$
$$\rightarrow Fe^+ + C_3H_8 + Xe \quad (2c)$$
$$\rightarrow FeH^+,\ FeCH_3^+,\ FeC_2H_5^+,\ FeXe^+ \quad (2d)$$

The guided-ion beam mass spectrometer on which these experiments were performed has been described previously.[3-5] Parent ions are formed in a meter-long flow tube[5] by termolecular collisions between Fe^+ (created in a DC discharge[6]), propane, and the He carrier gas. The complexes then undergo ~10^5 thermalizing collisions. The ions are mass and energy selected and then interact with Xe under single-collision conditions inside an octopole ion trap.[3,4] Reactant and product ions are mass analyzed and detected and their intensities converted to cross sections.[3]

Results of this threshold collisional activation (TCA) experiment are shown in Figure 1. The lowest energy processes are reactions 2a and 2b, while the major process is reaction 2c. The products of reaction 2d are also observed, which except for $C_3H_7^+$ and $FeXe^+$ are the same as those of reaction 1c. This correspondence indicates that reaction 2 is occurring on the same global PES as the bimolecular system. The dominance of reaction 2c suggests a $Fe^+\cdot C_3H_8$ structure for the parent ion since simple cleavage processes should be the main dissociation pathways at high collision energies. This conclusion is supported by recent work on TCA of $Fe^+\cdot C_2H_6$[7] that indicates that insertive structures have very different fragmentation patterns than simple adducts.

Quantitative information regarding reaction 2 can be obtained by measuring the product thresholds.[8] This analysis yields a threshold for process 2c of 0.82 ± 0.07 eV (19 ± 2 kcal/mol). Given the $Fe^+\cdot C_3H_8$ structure for the parent ion, this energy corresponds to the depth of the ion induced dipole well. This value can be verified by measuring the threshold for $FeCH_3^+$ formation, 2.17 ± 0.09 eV (50 ± 2 kcal/mol). Combined with $D°[Fe^+(^6D)–CH_3]$ = 58 ± 2 kcal/mol[2] and $D°(CH_3–C_2H_5)$ = 88 kcal/mol,[10] this threshold implies $D°[Fe^+(^6D)–C_3H_8]$ = 20 ± 3 kcal/mol, consistent with the directly measured value. Ad-

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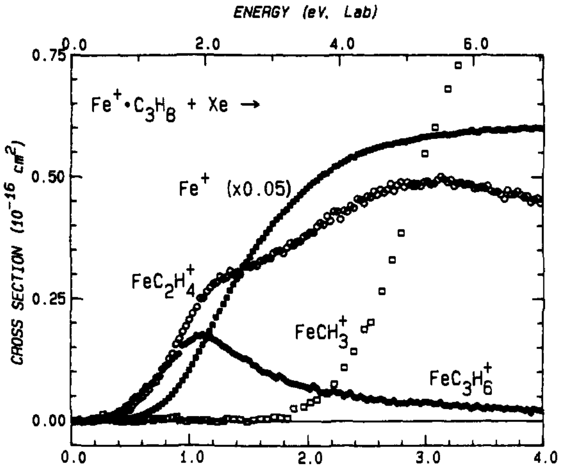

Figure 1. Cross sections for TCA of $Fe^+{\cdot}C_3H_8$ as a function of relative energy (lower x axis) and laboratory energy (upper x axis).

ditional experiments also imply that the parent ion derives from the $Fe^+(^6D,3d^64s)$ ground state rather than the $Fe^+(^4F,3d^7)$ first excited state. Specifically, recent measurements find that bond energies for Co^+–alkane complexes are consistently stronger than the analogous Fe^+–alkane species,[7,9] contrary to the similar alkane bond strengths expected for $Co^+(3d^8)$ and $Fe^+(3d^7)$.

Since reactions 1a and 1b (which are exothermic by 19 and 11 ± 5 kcal/mol,[10-12] respectively) exhibit no activation barriers,[2] reactions 2a and 2b must have lower thermodynamic thresholds than process 2c, as is evident from Figure 1. Analyses of these two products find a threshold of 0.47 ± 0.12 eV (11 ± 3 kcal/mol) for both processes, even though reactions 2a and 2b have different reaction enthalpies, ~0 and 8 kcal/mol, respectively, given $D^\circ(Fe^+{-}C_3H_8) = 19$ kcal/mol. Clearly, the observed threshold for reaction 2a is *not* the thermodynamic threshold, but rather the activation barrier associated with the rate-limiting step in the bimolecular process. It seems likely that this is also true for reaction 2b. In analogy with recent work on the Co^+ + propane system (based on completely different experimental techniques),[13] we propose that this barrier corresponds to the activation of a C–H bond of propane by Fe^+.

Further insight into the PES can be obtained from the kinetic energy dependence of reactions 2a and 2b. For the bimolecular system, reaction 1a is favored by a factor of 3 at all kinetic energies for both the ^6D and ^4F electronic states of Fe^+,[2] consistent with the overall thermodynamics. In contrast, the branching ratio of reactions 2a and 2b is highly energy dependent. At the lowest energies, reaction 2b is slightly favored, indicating that the product branching ratio is under kinetic control or that reaction 2b has a slightly lower threshold. Cross sections for both $FeC_2H_4^+$ and $FeC_3H_6^+$ exhibit a sudden change at ~1 eV. Since dissociation of these products cannot begin until 1.7 and 2.1 eV,[12] respectively, this abrupt change must be due to competition with direct dissociation, reaction 2c. Above this energy, cross sections for reactions 2a and 2b deviate strongly from one another, suggesting that a new pathway for reaction 2a (but not reaction 2b) becomes energetically accessible. An obvious choice is C–C bond activation. This then implies that the 11 kcal/mol activation barrier corresponds to an initial primary C–H bond activation step which can lead to both reactions 2a and 2b. Secondary C–H bond activation is also presumably occurring but apparently exhibits no independent feature in the TCA spectrum. The insensitivity of the branching ratio of reactions 1a and 1b to kinetic energy can be explained, since in reaction 1 (but *not* reaction 2), the reactants enter with enough energy to surmount either of the two activation barriers. These details are again similar to those suggested for reaction of Co^+ with C_3H_8.[13]

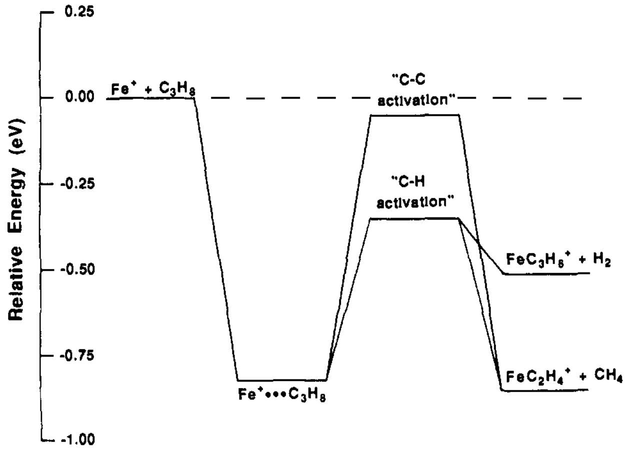

Figure 2. Thermodynamics of the Fe^+–propane potential energy surface. The "C–C activation" barrier is derived by scaling the cross section for reaction 2b to that of reaction 2a and fitting a threshold to the remainder.

The combination of all these results leads to the PES shown in Figure 2. This diagram clearly does not indicate all of the complications of the system, in particular the surfaces of differing spins that arise from the two lowest energy states of Fe^+.[2] Further work to probe the PES of this interesting reaction system is underway.[11] Such studies will include examination of the reverse of reactions 2a and 2b and, if possible, TCA of other purported intermediates on the PES.

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Primary and Secondary Oxygen-18 Isotope Effects in the Alkaline and Enzyme-Catalyzed Hydrolysis of Phosphotriesters

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Phosphotriester hydrolysis occurs by an associative mechanism with nucleophilic attack of hydroxide.[1] This associative process can occur via two limiting mechanistic alternatives: the formation

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