Thermochemistry and Structures of FeC₃H₆⁺: Metallacycle and Metal–Alkene Isomers

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Threshold collision-induced dissociation in a guided ion beam mass spectrometer is used to determine thermochemistry and structure for the Fe^+-alkene and metallacyclobutane structures of $FeC_3H_6^+$. A flow tube source (which ensures thermalization) is used to produce $FeC_3H_6^+$ as the adduct of Fe^+ with cyclopropane or propene, or by reaction of Fe^+ with propane or cyclobutanone. Differences in reactivity and thermochemistry of ions produced in different ways along with results of the bimolecular reactions of Fe^+ with cyclopropane and propene are used to infer structural differences. We determine 0 K bond dissociation energies of 39.6 ± 1.5 kcal/mol for Fe^+·propene, 31.8 ± 1.0 kcal/mol for the metallacycle to dissociate to Fe^+ + cyclopropane, and 82.6 ± 1.5 kcal/mol for Fe^+–CH_2. Arguments are also presented for elimination of ethylidene from Fe^+·propene, and the threshold for this process provides the first experimental measurement of the $\Delta_f H°_0$ of CH_3CH (ethylidene), 73 ± 7 kcal/mol.

Introduction

One important problem in chemistry is determining the structure (both molecular and electronic) and thermochemistry of reactive intermediates. In the area of organometallic chemistry, a better understanding of these intermediates could ultimately help achieve such diverse ends as more intelligent catalyst design and more efficient synthetic strategies. Precisely because these intermediates are so reactive, this kind of information is difficult to obtain by standard techniques. In the past decade, mass spectrometric techniques have seen wide use as a means of attacking these problems.[1] By removing the active species from solution and isolating it from other molecules, complications such as solvent effects and the extreme reactivity of these unsaturated species are removed. Mass spectrometry in particular provides a convenient way of identifying species of interest by mass and can even be used as a structural probe to distinguish isomers.[2]

Structure determination of ions is an application of mass spectrometry of long standing and wide use.[2] The method typically used in analytical mass spectrometry is to ionize a compound, observe the products of its decomposition, and infer structure from the fragmentation pattern. While the traditional method of producing ions is 70-eV electron impact, in recent years, other methods, such as fast atom bombardment, field ionization, and secondary ion mass spectrometry, have come into wide use for volatilizing and ionizing delicate molecules and polymers. Structure determination from fragmentation patterns of the metastable ions thus produced has been applied to metal ion–organic molecule systems.[3] An allied method of probing ion structure is collision-induced dissociation (CID), again inferring structure from the observed fragmentation patterns. Most CID structural studies are performed at very high collision energies (on the order of several kilovolts).[4] An example of this kind of study in an organometallic system is the report by Larsen and Ridge[5] of high-energy (8-kV) dissociation of Fe^+ complexed with alkanes, alkenes, and carbon monoxide and of Peake, Gross, and Ridge[6] of the CID of Fe^+-alkene complexes.

Low-energy CID, which is generally done at energies not exceeding volts, can also be used as a structural probe that should be more directly relevant to ion–molecule reaction chemistry.[7] Freiser and co-workers[8,9] have used low-energy CID in a Fourier transform ICR mass spectrometer to probe the structure of transition metal ion complexes such as M^+-alkene and metallacycle ions (including M = Fe, the specific subject of this report).

Studies by van Koppen et al.[10] have also probed the structures of $FeC_3H_6^+$ ions by using both KERD analyses and high-energy CID. This latter study is the only one of the three to provide any thermochemical information, although the unusual shapes of the KERDs prevented them from making anything other than "rough estimates" of the thermochemistry of the Fe^+·propene and metallacycle structures of $FeC_3H_6^+$.

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Because the internal energy of the parent ions is poorly characterized and because the collisions in the high-energy experiments take place at energies much higher than those needed to dissociate the ion, the direct relevance of these studies to the work here may be limited. The issue of characterizing the internal energy of the parent ion is an important one for structure determination, as a highly vibrationally excited ion may not have a single "structure" to be probed. In the present study, the use of a high-pressure ion source to control the internal energy eliminates this problem.

We have recently presented examples of our use of CID as a means of probing the thermochemistry of ligated Fe^+ complexes created in such a high-pressure source and of the cross-section modeling techniques we developed to analyze the observed cross section thresholds.[11-13] We have also presented an extension of this technique to the threshold collisional activation (TCA) of ion–molecule complexes in which collisions are used not only to cause simple dissociation but also to induce reactions at their thermodynamic thresholds.[12] In this paper, we report results of both types of experiments, simple CID and TCA, which we performed in order to probe the thermochemistry and structure of $FeC_3H_6^+$ ions. Ions having the $MC_nH_{2n}^+$ stoichiometry are of particular interest because they are commonly observed as products in the reactions of atomic metal ions with straight-chain, branched-chain, and cyclic organic species. For iron, reactions with straight- and branched-chain organic molecules appear to produce $FeC_nH_{2n}^+$ ions with Fe^+–alkene structures,[14,15] while reactions with cyclic compounds apparently yield metallacyclic species.[6,9b,16] Determining the thermochemistry of these species cannot be done directly from the bimolecular reactions of atomic ions with organic neutrals, since these reactions are invariably exothermic and proceed without any activation barriers. The only way of obtaining accurate thermochemistry (and, for that matter, structure) is to produce the ions and then probe them with additional reactions.

We undertook the present study for several reasons. First, we want to provide accurate thermochemistry for $FeC_3H_6^+$, both to compare with the results of van Koppen et al.[10] and to provide information for our studies of the Fe^+ + propane system.[12a,b,17] We also wanted to examine *energy-dependent* CID as a probe of the structure of transition metal ion complexes, since none of the previous studies made use of energy-dependent threshold CID to probe the structure and thermochemistry of $FeC_3H_6^+$ species.

Experimental Section

The guided ion beam instrument on which these experiments were performed has been described in detail previously.[18,19] Ions

are created in a flow tube source, described below, extracted from the source, accelerated, and passed through a magnetic sector for mass analysis. The mass-selected ions are then decelerated to the desired kinetic energy and focused into an octopole ion beam guide. This device uses radio-frequency electric fields to trap the ions in the radial direction and ensure complete collection of reactant and product ions. The octopole passes through a gas cell of effective length 8.6 cm that contains the neutral collision partner at a pressure sufficiently low that multiple ion–molecule collisions are improbable. The unreacted parent and product ions drift to the end of the octopole from which they are extracted, passed through a quadrupole mass filter for mass analysis, and detected with a secondary electron scintillation ion detector using standard pulse counting techniques. Raw ion intensities are converted to cross sections as described previously.[18] We estimate absolute cross sections to be accurate to ±20%, while relative cross sections are accurate to ±5%.

Laboratory (lab) energies are converted to energies in the center of mass (CM) frame by using the conversion $E_{CM} = E_{lab}M/(M + m)$, where m and M are the ion and neutral masses, respectively. The absolute energy scale and corresponding full width at half-maximum (fwhm) of the ion beam kinetic energy distribution are determined by using the octopole as a retarding energy analyzer as described previously.[18] The absolute uncertainty in the energy scale is ±0.05 eV (lab). The energy distributions are nearly Gaussian and have typical fwhms of 0.25–0.4 eV (lab).

Reactant ions are made in our flow tube source, described in detail previously.[19] Fe^+ is made by using a dc discharge source[11] consisting of a carbon steel cathode held at high negative voltage (typically 1.5–3 kV) over which a flow comprising approximately 90% He and 10% Ar passes. Ar^+ ions are accelerated toward the cathode, sputtering off ionic and neutral species. An appropriate source gas, either C_3H_8, propene, cyclopropane, or cyclobutanone, is added to the flow downstream of the discharge. $FeC_3H_6^+$ ions are then formed by bimolecular reactions or three-body collisions. At typical flow tube pressures of 0.5–0.6 Torr, the ions undergo on the order of 10^5 thermalizing collisions as they traverse the 1-m-long flow tube. Ions are extracted from the flow tube and gently focused through a 9.5-cm-long differentially pumped region before entering the rest of the instrument described above.

Before any experimental run, a high-energy (20–25-eV lab) CID spectrum with Xe was taken in order to make sure that no impurity ions were present in the parent ion beam. For some of the initial experiments, C_3H_8 was added to the flow tube. This method of producing $FeC_3H_6^+$ had the difficulty that interference from $^{54}FeC_3H_8^+$ was unavoidable, and insufficient quantities of $^{54}FeC_3H_6^+$ were made for detailed study. In cases where $^{56}FeC_3H_6^+$ made from dehydrogenation of propane was used as the parent ion, product $^{54}Fe^+$ was collected as well. In order to determine the relative amounts of $^{54}FeC_3H_8^+$ and $^{56}FeC_3H_6^+$ present in the parent beam, the magnitude of the $^{54}Fe^+$ cross section was compared to the known cross section for CID of $^{56}FeC_3H_8^+$.[12] Since the $^{54}Fe^+$ cross section measured in these cases was generally >60% of the magnitude of the $FeC_3H_8^+$ CID section, we conclude that the "$FeC_3H_6^+$" beam made by reaction of Fe^+ with propane actually comprised primarily $^{54}FeC_3H_8^+$, with less than 40% $^{56}FeC_3H_6^+$.

In order to make larger quantities of $FeC_3H_6^+$, propene was added to the flow tube through one of the side ports. The experimental results were independent of whether the propene was added 25 or 50 cm downstream of the dc discharge. The CID cross section was the same for $FeC_3H_6^+$ made from reaction with propane and as the propene adduct. The latter method was used for most of the experiments and produced sufficiently intense beams of $FeC_3H_6^+$ that we were able to collect minor products as well.

Ions with the presumed metallacyclic structure were also made in two ways. For some experiments, cyclobutanone was added to the flow tube. Fe^+ is known to exothermically eliminate CO from cyclobutanone,[9b,10] leaving behind an $FeC_3H_6^+$ ion. While there might conceivably be competition from $FeC_2H_2O^+$, which has the same mass as $FeC_3H_6^+$, neither previous study of the

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Table I. Vibrational Frequencies (cm⁻¹) Used in Equation 1 and in Deriving the 0 K Fe⁺–CH₂ BDE[a]

species	frequencies
propene[b]	174, 428, 578, 912, 920, 963, 991, 1045, 1171, 1297, 1378, 1420, 1443, 1470, 1650, 2871, 2932, 2954, 2991, 3013, 3090
Fe⁺—CH₂=CHCH₃	A: free propene + 100, 300, 500
	B: free propene + 100, 400, 700
	C: free propene + 300, 500, 700
Fe⁺CH₂CH₂CH₂	common frequencies: 535, 556, 627, 741, 749, 898, 926, 1001(2), 1219, 1222, 1223, 1257 (2), 1260, 1443, 1447, 2887, 2893, 2895, 2952, 2975, 2987[c]
	A: common frequencies + 1443
	B: common frequencies + 197
FeCH₂⁺	452.0, 623.9, 700.3, 1319.2, 2941.6, 3011.5[d]

[a] Degeneracies in parentheses. [b] Vibrational frequencies for free propene taken from: Sverdlov, L. M.; Kovner, M, A.; Krainov, E. P. *Vibrational Spectra of Polyatomic Molecules*; Wiley: New York, 1974. [c] Vibrational frequencies for Fe⁺·cyclopropane are taken from: Shimanouchi, T. *Table of Molecular Vibrational Frequencies*, Consolidated Vol. I; National Bureau of Standards: Washington, DC, 1972. Vibrational data for the Fe·cyclopropane adduct measured in an argon matrix from ref 23; see text and ref 10. [d] Reference 35.

reaction of Fe⁺ with cyclobutanone reported any observation of this product,[9b,10] and we saw no CID products implying its presence here. Most experiments were performed by using FeC₃H₆⁺ ions made from the reaction of Fe⁺ with cyclopropane added to the flow tube through one of the side ports. The latter method provided more intense beams, and no significant differences were found in the CID behavior of the FeC₃H₆⁺ ions made the two ways.

The bimolecular reactions of Fe⁺ with cyclopropane and propene were also performed and provide a useful counterpoint to the CID studies. For most experiments, Fe⁺ was made by surface ionization (SI). In this method, Fe(CO)₅ is admitted to the source chamber and directed at a Re filament resistively heated to about 2300 K. The compound decomposes, and Fe⁺ ions are believed to be formed with a Maxwell–Boltzmann distribution of electronic energies.[20] At 2300 K, this source will thus produce about 80% Fe⁺(⁶D, 4s3d⁶) ground state and 20% Fe⁺(⁴F, 3d⁷) first excited state. Some of the reactions with cyclopropane were done by using a drift cell (DC)[21] as the source of Fe⁺ ions, in which ions made by electron impact on Fe(CO)₅ are thermalized with about 1000 collisions with Ar atoms. This source is believed to produce >98% Fe⁺ in its ground electronic state.[21]

CID cross-section thresholds are modeled by using eq 1,[11] where E is the relative translational energy, E₀ is the reaction threshold at 0 K, σ₀ is an energy-independent scaling parameter, and the exponent n is treated as a variable parameter. In order to take

$$\sigma = \sigma_0 \Sigma_i g_i (E + E_i + E_{rot} - E_0)^n / E \qquad (1)$$

into account the thermal internal energies of the polyatomic parent ions, we include a summation over vibrational energy levels i with energies E_i and relative populations g_i. We use the Beyer–Swinehart algorithm[22] to calculate a Maxwell–Boltzmann distribution of vibrational energies at 300 K which is used for the factors g_i in eq 1. We also explicitly include the average rotational energy $(0.039 \text{ eV} = 3k_BT/2)$ of the reactant ions, E_{rot}. We have described this threshold modeling procedure in detail elsewhere.[11]

In the case of the Fe⁺·C₃H₆ complexes, there is very little information about the correct vibrational energies to include. We follow a procedure similar to that of van Koppen et al.,[10] in which we use the vibrational frequencies determined for the free ligand, and use values for the modes involving Fe⁺ that are at the limits of what is reasonable (Table I). For Fe⁺·cyclopropane, we assume a ferrocyclobutane structure and use frequencies for the Fe⁺-C modes taken from a matrix study of the Fe–cyclopropane complex.[23] The values used for the vibrational levels are summarized in Table I. Because these species have few low-frequency modes, incorporating the vibrational energy into the threshold model only increases the threshold determined by eq 1 by about 1 kcal/mol.

For several of the data are analyzed, there was a small residual background of ca. 0.05 Å² which was independent of energy or

xenon pressure. A similar nonzero background has been noted for transition-metal cluster ion dissociation in an instrument similar to the one on which these experiments were performed.[24] The lack of energy dependence implies that the background is not due to dissociation of metastable excited ions. We presume that it is due to ions excited by collisions outside of the gas cell as they traverse the instrument. These cross sections were modeled in two different ways. Either the background was simply subtracted out, or the fit was statistically weighted to ignore the background. The two fitting methods yield results that are the same to within experimental error.

The hydrocarbon gases were obtained from Matheson in high purity (>99%) and used without further purification. Cyclobutanone (99%, obtained from Aldrich) and Xe (99.995%, Air Products) were used without further purification except for multiple freeze–pump–thaw cycles to remove condensible impurities.

Results

Fe⁺ + Propene and Cyclopropane. As a starting point for understanding the Fe⁺–C₃H₆ reaction systems, we studied the bimolecular reactions of Fe⁺ (SI) with propene and cyclopropane. The presence of two electronic states in the Fe⁺ beam can make unambiguous threshold analysis difficult.[21,25-27] We have presented evidence elsewhere that any C–C or C–H bond activation intermediate arising from reactions of Fe⁺ is likely to be a quartet.[17] Thus, the ⁴F first excited state of Fe⁺ generally has been observed to react more efficiently than the ⁶D ground state.[17,21,25-28] The thermochemical analyses of most of the bimolecular reactions of Fe⁺ studied here assume that the reactivity at the experimentally observed threshold is due to Fe⁺(⁴F). In contrast to this general case, state-specific work with Fe⁺ + cyclopropane and ethylene oxide[29] has shown that both states react efficiently to form FeCH₂⁺, so the cross-section model for this product explicitly includes consideration of both electronic states of Fe⁺(SI).[30]

The major products for reaction with propene are shown in Figure 1. The only product observed at low energy is the adduct ion. While adduct ion formation is normally due to multiple collisions in the gas cell, data sets taken 2 years apart with gas cell pressures of 0.05 and 0.08 mTorr

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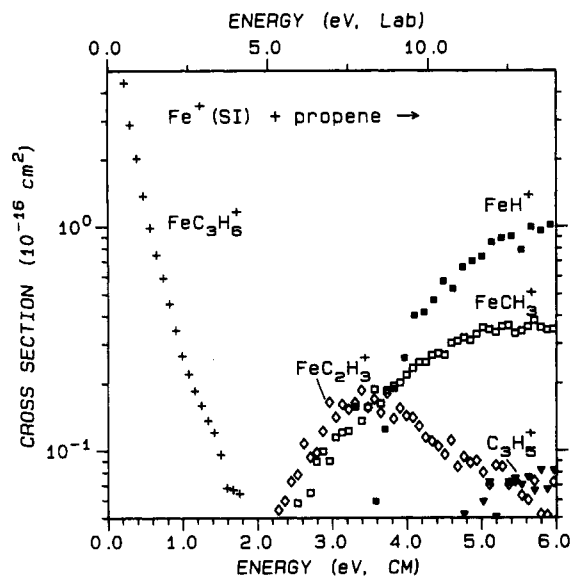
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Figure 1. Cross sections for reaction of Fe⁺(SI) with propene as a function of relative energy (lower x axis) and laboratory energy (upper x axis). Shown are the products with peak cross sections greater than 0.05 Å². Cross sections for adduct formation are indicated by "+", those for formation of FeH⁺ by solid squares, those for formation of FeCH₃⁺ as open squares, those for formation of FeC₂H₃⁺ by open diamonds, and those for formation of C₃H₅⁺ as solid inverted triangles.

Figure 2. Cross sections for the reaction of Fe⁺(SI) with cyclopropane as a function of relative energy (lower x axis) and laboratory energy (upper x axis). Shown are the products with peak cross sections greater than 0.05 Å². Cross sections for formation of FeH⁺ are shown by solid squares, those for formation of FeCH₂⁺ as triangles, those for formation of FeCH₃⁺ as open squares, and those for formation of C₃H₅⁺ as inverted triangles.

had exactly the same cross-section magnitudes. This independence of cross-section magnitude on the pressure of the neutral gas indicates that some fraction of adducts formed in a single collision live long enough to reach the detector (about 10 μs). The adduct ion is formed at 5 ± 2% of the collision cross section[31] at the lowest energies (ca. 0.05 eV). It falls off as $E^{-1.1\pm0.2}$ below 0.4 eV and $E^{-2.5\pm0.2}$ at higher energies. Two other products, FeCH₂⁺ and FeC₂H₂⁺, were also observed but are not shown in Figure 1, due to their small magnitudes (peak cross sections of about 0.05 Å²). The former ion only appears at high energy. The latter product has an unusual shape, arising from an apparent threshold of about 1–1.5 eV, falls off above about 3 eV, and then begins to rise again about 5 eV. This behavior is consistent with formation of FeC₂H₂⁺ + CH₄ at low energy and FeC₂H₂⁺ + CH₃ + H at elevated energy.

Figure 2 shows cross sections for reaction of Fe⁺(SI) with cyclopropane. A major product of reaction is FeCH₂⁺. This product rises from a threshold well below 1 eV to a peak cross section of about 7 Å². FeH⁺, FeCH₃⁺, and C₃H₅⁺ arise at higher energies and have much smaller cross sections. Not shown in Figure 2 are a wealth of minor products such as FeC₂Hₓ⁺ (x = 2,3) and C$_y$H$_z$⁺ (y = 1–3, $y \le z \le y + 2$). Most of these arise from high-energy decomposition of the major products, and except for FeC₂H₃⁺, C₃H₃⁺, and C₂H₃⁺, which have peak cross sections of about 0.1 Å², all of these minor products have peak cross sections of ≤0.05 Å².

Fe⁺·Propene + Xe. Cross sections for the major products of the reaction of Xe with FeC₃H₆⁺ made by adding propene to the flow tube are shown in Figure 3. The predominant product at all energies is CID to form Fe⁺. This product arises from an apparent threshold between 1 and 2 eV to reach a maximum cross section of about 8 Å² above 4 eV, above which it does not decline
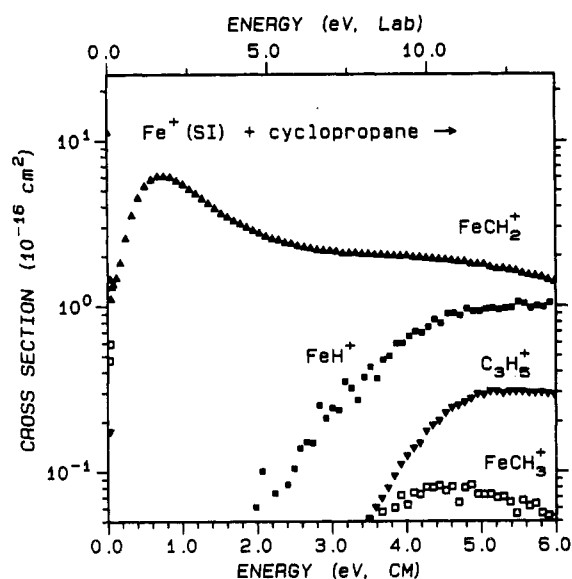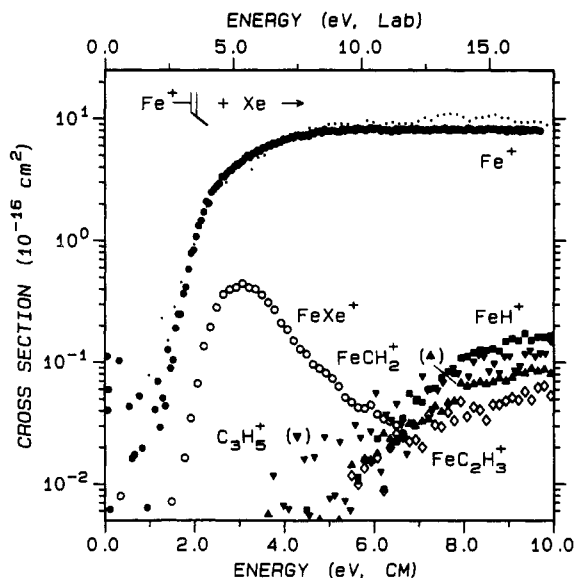

Figure 3. Cross sections for CID of FeC₃H₆⁺ (Fe⁺·propene) as a function of relative energy (lower x axis) and laboratory energy (upper x axis). Collision-induced dissociation to form Fe⁺ is shown as solid circles, and ligand exchange as open circles. Cross sections for formation of FeH⁺ are shown as solid squares, FeCH₂⁺ as solid triangles, FeC₂H₃⁺ as open diamonds, and C₃H₅⁺ as inverted triangles. For comparison, cross sections for CID of FeC₃H₆⁺ produced by reaction of Fe⁺ and C₃H₈ in the flow tube, normalized as described in the text, are shown as small dots.

appreciably. At low energy, some ligand exchange to form FeXe⁺ is observed. Although the logarithmic y scale on which these results are plotted can be deceptive because of broadening due to the kinetic energy distributions of the ion beam and neutral gas,[18,19] careful examination of the Fe⁺ and FeXe⁺ cross sections shows that the latter does rise from a threshold below that for simple CID. At energies above about 5 eV, several other products, FeH⁺, FeCH₂⁺, FeC₂H₃⁺, and C₃H₅⁺, are seen. All four reach peak cross sections of <0.2 Å² above 10 eV. Two interesting contrasts between the CID and bimolecular reac-

(31) Gioumousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *29*, 294. α(propene) = 6.04 Å³: Rothe, E. W.; Bernstein, R. B. *J. Chem. Phys.* **1959**, *31*, 1619.
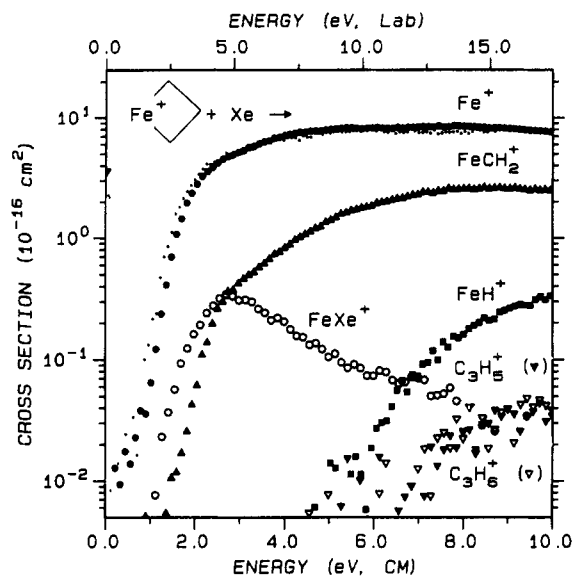
Figure 4. Cross sections for CID of $FeC_3H_6^+$ (Fe^+·cyclopropane, concluded to have a metallacyclobutane structure) as a function of relative energy (lower x axis) and laboratory energy (upper x axis). CID to form Fe^+ is shown as solid circles and ligand exchange as open circles. Cross sections for formation of FeH^+ are shown as solid squares, $FeCH_2^+$ as solid triangles, $C_3H_5^+$ as solid inverted triangles, and $C_3H_6^+$ as open inverted triangles. For comparison, cross sections for CID of $FeC_3H_6^+$ formed by reaction of Fe^+ and cyclobutanone in the flow tube are shown as small dots.

Table II. 0 K Literature Thermochemistry Used in This Paper[a]

species	$\Delta_f H^\circ_0$, kcal/mol	IE, eV
CH_2	92.2 ± 1.0	
CH_3	35.62 ± 0.2	
C_2H_2	56.35 ± 0.19	
C_2H_3	72.7 ± 0.8^b	
C_2H_4	14.58 ± 0.07	
C_3H_6 (propene)	$8.3 \pm 0.2^{c,d}$	9.73 ± 0.02^c
C_3H_6 (cyclopropane)	$16.8 \pm 0.2^{c,e}$	9.86^c
Fe	98.73 ± 0.06	7.90^f
H	51.6	

[a] Unless otherwise stated, all information in this table is taken from: Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* 1985, *14*, Supp. No. 1 (JANAF Tables). [b] Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* 1990, *112*, 5750. [c] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* 1988, *17*, Supp. No. 1 (GIANT Tables). [d] Calculated, assuming ideal gas behavior, from $\Delta_f H^\circ_{298}$ of 4.8 ± 0.2 given in ref c and vibrational frequencies given in Table I. [e] Calculated, assuming ideal gas behavior, from $\Delta_f H^\circ_{298}$ of 12.7 ± 0.2 kcal/mol given in ref c and vibrational frequencies given in: Shimanouchi, T. *Table of Molecular Frequencies*, Consolidated Vol. I; National Bureau of Standards: Washington, DC, 1972. [f] Corliss, C.; Sugar, J. *J. Phys. Chem. Ref. Data* 1985, *14*, Supp. No. 2.

tions are that $FeCH_2^+$, a product of the former reaction, is very small in the latter and that $FeCH_3^+$, a major product of the bimolecular reaction, is not observed as a product from CID. What makes the latter observation more unusual is that $FeC_2H_3^+$, which has CH_3 as the neutral product, is observed as a product of both reactions. The origins of these contrasting behaviors are discussed below.

Also shown in Figure 3 is dissociation to Fe^+ for the $FeC_3H_6^+$ ion made by adding propane to the flow tube. Its absolute cross section and energy dependence are the same as that for the Fe^+·propene adduct within experimental error, implying that the two have the same structure and degree of thermalization.

Fe^+·Cyclopropane + Xe. Results from CID of $FeC_3H_6^+$ formed by adding cyclopropane to the flow tube are shown in Figure 4. (We use the designation of Fe^+·cyclopropane to indicate the means of producing the $FeC_3H_6^+$ species formed and not to suggest a specific structure. A detailed interpretation of the results that suggests a metallacycle structure for this species is provided in the discussion section.) Once again, the major process at all energies is dissociation to form Fe^+. This cross section arises from an apparent threshold between 0 and 1 eV, somewhat lower than the apparent threshold for CID of Fe^+·propene, and peaks at about 8 Å² above 5 eV. As with Fe^+·propene, ligand exchange arises from a threshold slightly below that of CID (again, the logarithmic y axis on which the cross sections are plotted is deceptive in this respect). High-energy products are FeH^+, $C_3H_5^+$, and $C_3H_6^+$, all of which rise from energies above 4 eV to peak cross sections above 10 eV of 0.3 Å² for FeH^+ and about 0.04 Å² for the other two products. This product distribution is quite similar to that for the bimolecular reaction, especially in that $FeCH_2^+$ is the major reaction product in both systems.

Also shown in Figure 4 is dissociation to Fe^+ for the $FeC_3H_6^+$ ion made by adding cyclobutanone to the flow tube. Its absolute cross section and energy dependence are the same as that for Fe^+·cyclopropane within experi-

mental error, implying that the two have the same structure and degree of thermalization.

Contrast of the CID Experiments. There are three major differences between the product distribution for CID of Fe^+·cyclopropane and that for Fe^+·propene. The most obvious is the difference in the cross section for formation of $FeCH_2^+$. While for Fe^+·propene $FeCH_2^+$ only appears at high energy with a small cross section, it is a major product in the CID spectrum of Fe^+·cyclopropane, rising from an apparent threshold between 1 and 2 eV to a peak of about 2.5 Å² above 7 eV. The other differences are that $FeC_2H_3^+$, a high-energy product of CID of Fe^+·propene, is not observed for Fe^+·cyclopropane, while $C_3H_6^+$ is observed as a product from Fe^+·cyclopropane but not from Fe^+·propene. This last difference is somewhat surprising, since the ionization energies of cyclopropane and propene are similar (Table II), and so the probability of charge transfer should be nearly equal in the two systems. It is possible that $C_3H_6^+$ is being produced from Fe^+·propene, but with a cross section below our detectability limit of about 0.01 Å².

Ligand Exchange with CO. As a further comparison between the $FeC_3H_6^+$ ions prepared as Fe^+·propene or Fe^+·cyclopropane, the ligand-exchange reaction with CO was also studied. The results are shown in Figure 5. As can be seen, while the $FeC_3H_6^+$ ions made in the two different ways have the same peak cross section for ligand exchange of about 0.06 Å², Fe^+·cyclopropane has a noticeably lower threshold for ligand exchange than does Fe^+·propene, consistent with the relative thresholds for dissociation of the two ions as shown in Figures 3 and 4. The ligand-exchange behavior and its relevance to the structural probes are discussed in more detail below.

Comparisons to Other CID Measurements. While the results of the high-energy CID experiments[6,10] may not necessarily be directly relevant to the present experiment, there are some interesting similarities between the results. The earlier studies and the present one all find that Fe^+·cyclopropane is much more prone to dissociate to $FeCH_2^+$ than is Fe^+·propene. This result implies a structural difference in the $FeC_3H_6^+$ ions prepared in the two ways. On the other hand, high-energy CID produces
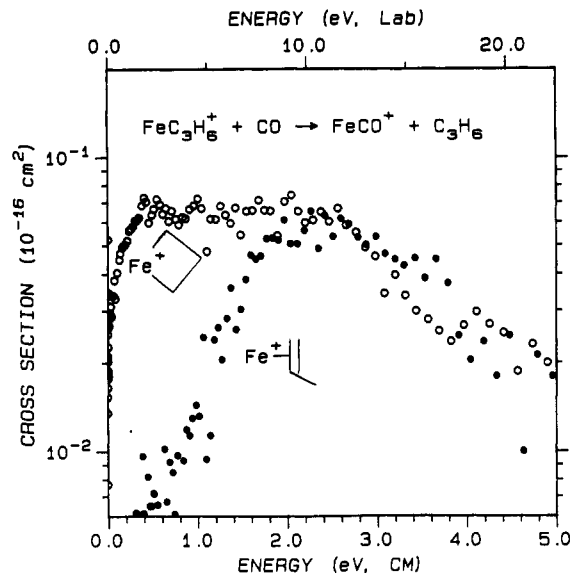
Figure 5. Cross sections for ligand exchange with CO as a function of relative energy (lower x axis) and laboratory energy (upper x axis). Cross sections for ligand exchange with the Fe⁺·propene adduct are shown as solid circles and those for ligand exchange with the Fe⁺·cyclopropane metallacycle as open circles.
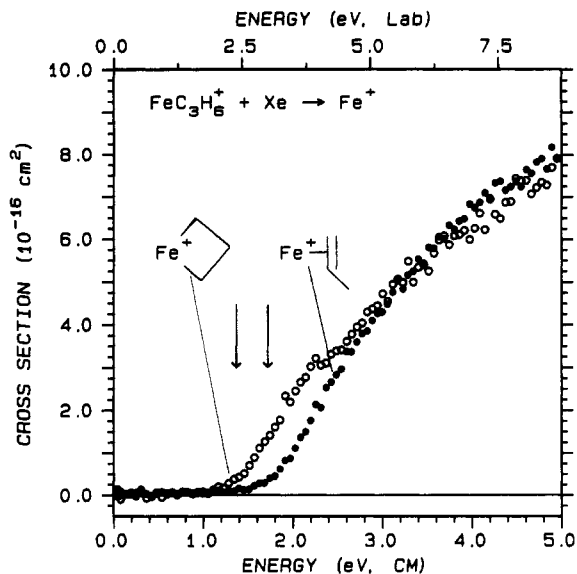

Figure 6. Comparison of the threshold cross sections for CID of the Fe⁺·cyclopropane metallacycle (open circles) and of the Fe⁺·propene complex (solid circles). The vertical arrows show the respective dissociation thresholds of 1.38 and 1.72 eV.

a much wider array of dissociation products (e.g., $FeC_3H_x^+$ and $FeC_2H_x^+$) than is seen here. The larger number of products seen in those experiments is simply a result of their having more energy available for the dissociation.

In their low-energy FTMS-CID experiment, Jacobson et al.[9b] also observed Fe⁺ and $FeCH_2^+$ as the dissociation products of $FeC_3H_6^+$ generated from reaction of Fe⁺ with cyclobutanone. They reported a similar ratio of Fe⁺: $FeCH_2^+$ formation to ours when properly compared on a CM energy scale and that the relative amount of $FeCH_2^+$ increases with increasing translational energy.

CID as a Probe of Thermochemistry

Fe⁺-C₃H₆. Determination of the bond dissociation energies (BDEs) of the $FeC_3H_6^+$ complexes is straightforward in principle. Assuming that the parent ions are thermal, the threshold for dissociation should be equal to the BDEs. Unfortunately, for $FeC_3H_6^+$ ions (and indeed for any ligated Fe⁺ ion), the matter is complicated by the question of to what electronic state of Fe⁺ the ions dissociate.[11,13,32] Because Fe⁺(⁴F) is only about 0.25 eV higher in energy than Fe⁺(⁶D), it is not always immediately obvious which state will correlate to the ground state of the $FeC_3H_6^+$ complex. To our knowledge, no detailed calculations on the electronic structures of the $FeC_3H_6^+$ ions exist. We have argued that any ion with two covalent bonds to an Fe⁺ center should have a quartet spin, implying that the $FeC_3H_6^+$ metallacycle structure is a quartet and thus might preferentially dissociate to the ⁴F excited state of Fe⁺. On the other hand, we have observed previously[29] that even the ⁶D ground state of Fe⁺ can react with cyclopropane efficiently to form $FeCH_2^+$ + C_2H_4, which have quartet and singlet spin states, respectively, implying that whatever its ground electronic state Fe⁺·cyclopropane can efficiently dissociate to Fe⁺(⁶D). We therefore assume that we are observing dissociation of Fe⁺·cyclopropane to Fe⁺(⁶D).

Determining a priori the electronic spin of Fe⁺·propene is also difficult. Like CO and H_2O, we expect it to bond datively to Fe⁺. As ab initio calculations[33] predict a sextet

Table III. Bond Dissociation Energies at 0 K

| species | $D°_0$, kcal/mol | |
	this study	prior measurements
Fe⁺—CH₂=CHCH₃	39.6 ± 1.5[a]	37 ± 5[b]
Fe⁺CH₂CH₂CH₂	31.8 ± 1.0[c]	30 ± 5[b,d]
Fe⁺—CH₂	82.6 ± 1.5	94 ± 5[e]
	82.6 ± 0.8[f]	80.8 ± 5.1[g]
Fe⁺—C₂H₃	60.2 ± 2.3[h]	

[a] $n = 1.5 ± 0.1$ and $\sigma_0 = 7.2 ± 2.5$ (eq 1). [b] Reference 10. [c] Dissociation to Fe⁺ + cyclopropane; $n = 1.2 ± 0.1$, $\sigma_0 = 5.1 ± 2.9$ (eq 1). [d] These authors originally reported dissociation to Fe⁺ + trimethylene; the value reported here is calculated from their reported $\Delta_f H°_0$ of 268 ± 5 kcal/mol for the $FeC_3H_6^+$ ion. [e] Reference 15. Value converted to 0 K from the originally reported 298 K BDE of 95 ± 5 kcal/mol. [f] From reaction of Fe⁺ + cyclopropane. Value converted to 0 K from the measured 298 K BDE of 83.9 ± 0.8 kcal/mol. [g] Reference 37. Value converted to 0 K from the originally reported 298 K BDE of 82.1 ± 5.1 kcal/mol; see text. [h] 298 K.

ground state for Fe(H₂O)⁺ but a quartet ground state for FeCO⁺, there appears to be no way to predict the ground electronic state of Fe(propene)⁺ without extensive calculations.

The threshold regions for CID to form Fe⁺ for ions made from addition of propene to the flow tube are compared with those made by addition of cyclopropane in Figure 6. Our measured thresholds of 1.72 ± 0.07 eV (39.6 ± 1.5 kcal/mol) and 1.38 ± 0.04 eV (31.8 ± 1.0 kcal/mol) for the propene and cyclopropane complexes, respectively, lead directly to the thermochemistry given in Table III. Our measured BDEs are in quite good agreement with the values derived from the KERD studies of van Koppen et al.[10] An earlier KERD study[34] had measured the Co⁺·propene BDE as 48 ± 3 kcal/mol. In general, BDEs for datively bound ligands to Co⁺ tend to be larger than the corresponding Fe⁺-ligand BDEs, as we discuss in detail elsewhere.[13] In the present case, the Co⁺-propene BDE is higher than the Fe⁺-propene BDE presumably because

(32) Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1989**, *90*, 7264. Barnes, L. A.; Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1990**, *93*, 609.

(33) Fe(H₂O)⁺: Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1989**, *90*, 7264; **1990**, *92*, 1876. FeCO⁺: Barnes, L. A.; Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1990**, *93*, 609.

(34) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; van Koppen, P. A. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1988**, *110*, 1.
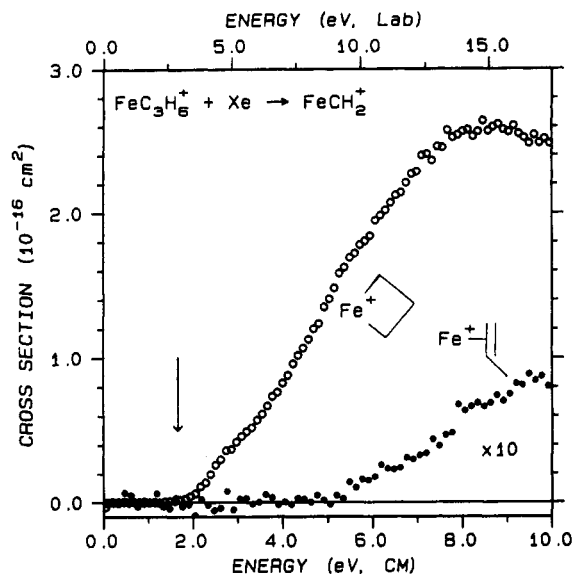
Figure 7. Comparison of the cross sections for formation of $FeCH_2^+$ from collisional activation of the Fe^+·cyclopropane metallacycle (open circles) and of the Fe^+·propene complex (closed circles, multiplied by 10). The vertical arrow shows the threshold for the former reaction of 1.67 eV.

the ground electronic state of Co^+ is d^8 as opposed to the $4s3d^6$ ground state of Fe^+. The 4s electron on the Fe^+ ion can lead to increased repulsion between the ligand and the Fe^+ ion and lower the BDE relative to that for Co^+ which lacks the 4s electron. We take our observation of a lower Fe^+-propene than Co^+-propene BDE as evidence that we are observing dissociation to ground state $Fe^+(^6D)$ in this case as well.

$FeCH_2^+$. A primary thermodynamic quantity of interest that can be obtained from examining the reaction of Fe^+ with cyclopropane (Figure 2) is the bond dissociation energy of $FeCH_2^+$. This product is formed in the endothermic reaction 2 and has a threshold that was deter-

$$Fe^+ + c\text{-}C_3H_6 \rightarrow FeCH_2^+ + C_2H_4 \qquad (2)$$

mined by using a variation of eq 1 in which the actual populations and energies of the various electronic states and individual J levels of Fe^+ were explicitly included.[20] In this case, $D°(Fe^+\text{-}CH_2)$ is calculated by subtracting the measured threshold for reaction 2, 0.360 ± 0.04 eV for $Fe^+(^6D)$, from the enthalpy for dissociating cyclopropane to CH_2 and C_2H_4, 4.00 eV at 298 K. This procedure yields a 298 K BDE of 3.64 ± 0.04 eV (83.9 ± 0.8 kcal/mol).

We can also obtain a value for $D°_0(Fe^+\text{-}CH_2)$ from the threshold for forming $FeCH_2^+$ from Fe^+·cyclopropane, reaction 3. The threshold region for this reaction is shown

$$Fe^+\cdot(c\text{-}C_3H_6) + Xe \rightarrow FeCH_2^+ + C_2H_4 + Xe \qquad (3)$$

in Figure 7. In the absence of a barrier to this reaction above its endothermicity, the Fe^+-CH_2 BDE is simply the sum of the Fe^+-cyclopropane BDE (1.38 ± 0.04 eV) and the enthalpy for dissociating cyclopropane into CH_2 and C_2H_4 (3.90 ± 0.04 eV at 0 K; Table II) minus the measured threshold for reaction 3, 1.70 ± 0.03 eV. This procedure yields $D°_0$ (Fe^+-CH_2) = 3.58 ± 0.07 eV (82.6 ± 1.5 kcal/mol) (Table III).

To test the accuracy of the BDEs measured in the two ways, we have to convert them to the same temperature. To make the conversion properly, one needs to know the vibrational frequencies of $FeCH_2^+$. Not surprisingly, no one has either measured or calculated these values in the gas phase. We therefore approximate the $FeCH_2^+$ vibra-

tional modes by using the values reported by Hauge et al.[35] for neutral $FeCH_2$ in an argon matrix. Using their vibrational frequencies (Table I), we can convert the 298 K BDE (measured from the threshold of reaction 2) to a 0 K value of 3.58 ± 0.04 eV (82.6 ± 0.8 kcal/mol), which matches the 0 K BDE determined from the threshold of reaction 3. Having approximated the vibrational frequencies and ignored the electronic contribution to the heat capacity undoubtedly introduces some error in this conversion, but this error is not expected to be large. For instance, if the true gas-phase vibrational frequencies differ from those measured in the Ar matrix by 20%, the calculated 0 K BDE would differ from the true one by 0.15 kcal/mol (0.007 eV) or less. The agreement between the values obtained from reactions 2 and 3 also implies that the reactions being observed in the present experiment are all occurring on the ground state surface to produce ground state products.

There are two prior values for $D°(Fe^+\text{-}CH_2)$ in the literature (Table III). Armentrout et al.[36] obtained a 298 K value of 95 ± 5 kcal/mol (which can be converted to a 0 K BDE of 94 ± 5 kcal/mol) from their ion beam study of the reaction of Fe^+ with C_2H_4. Because they did not take into account electronic effects and because the cross section for this reaction rises slowly from its threshold making analysis difficult, their value may not be accurate. Freiser and co-workers[37] obtained a 298 K value for this BDE of 82 ± 5 kcal/mol (which can be converted to a 0 K BDE of 81 ± 5 kcal/mol) by measuring the photodissociation threshold for $FeCH_2^+$.

Fe^+-C_2H_3. One other BDE that can be determined from the bimolecular reaction of Fe^+ with propene is that for Fe^+-C_2H_3, formed by process 4. We can use our observed

$$Fe^+ + C_3H_6 \rightarrow FeC_2H_3^+ + CH_3 \qquad (4)$$
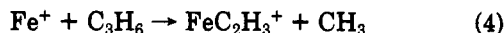
threshold for formation of $FeC_2H_3^+$, 1.56 ± 0.1 eV, along with 298 K literature thermochemistry to derive a BDE for $Fe^+(^4F)$-C_2H_3 of 65.7 ± 2.3 kcal/mol, and hence of 60.2 ± 2.3 kcal/mol for $Fe^+(^6D)$-C_2H_3. We report a somewhat less precise BDE for Fe^+-C_2H_3 than for the others given here because it was determined from a single data set.

CH_3CH (Ethylidene). A cursory glance at Figure 7 is sufficient to ascertain that the formation of $FeCH_2^+$ from Fe^+·propene is vastly different from its formation from Fe^+·cyclopropane. The cross section is smaller by a factor of about 25 and rises from a threshold near 5 eV. If the neutral product of this reaction were ethene, then we would expect the threshold for $FeCH_2^+$ formation to be 2.4 ± 0.1 eV. Clearly, this process is not what is occurring. Neither does formation of $FeCH_2^+$ from $FeC_3H_6^+$ correspond to dissociation of $FeCH_2^+ + C_2H_2 + H_2$ or $FeCH_2^+ + C_2H_3$ + H, since these processes should have thresholds of 4.2 and 7.1 eV, respectively. While it is possible that there is a 17 kcal/mol barrier to formation of $FeCH_2^+ + C_2H_2$ + H_2, such a process requires an $FeCH_4^+$ or $FeC_3H_4^+$ precursor, neither of which we observe. There could also be a 50 kcal/mol barrier to formation of $FeCH_2^+ + C_2H_4$ from $FeC_3H_6^+$, but such a large activation barrier seems unlikely for an ion–molecule reaction.

One possible explanation for the observed behavior is that the neutral product is not ethene, but rather the

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(36) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.

(37) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 2537. Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086.

product of simply cleaving the C–C double bond of propene to yield CH_3CH (ethylidene) in reaction 5. Although

$$Fe^+\cdot(CH_2\!\!=\!\!CHCH_3) + Xe \rightarrow FeCH_2^+ + CHCH_3 + Xe \tag{5}$$
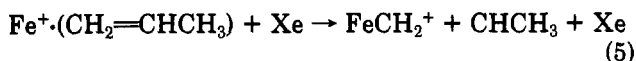
ethylidene has been reported in surface studies as an intermediate in ethene breakdown[38] and as a ligand in condensed-phase organometallic complexes,[39] surprisingly, we could not find any experimental values in the literature for its heat of formation. Its heat of formation has been the subject of some theoretical consideration. Two MNDO calculations derived the widely varying values for $\Delta_f H$-(CH_3CH) of 88.5[40] and 68.4 kcal/mol.[41] The second study provided no information about the source of the discrepancy. Theoretical interest in ethylidene has also been stimulated by its being a saddle point on the C_2H_4 potential energy surface. Thus, two ab initio calculations have been carried out on the relative stabilities of ethylidene and ethene. Pople et al.[42] calculated that triplet ethylidene is 67.2 kcal/mol less stable than ethene, while Trinquier[43] calculated the difference to be 65.3 kcal/mol. Given the 0 K heat of formation for ethene of 14.58 kcal/mol (Table II), these calculations thus predict that $\Delta_f H(CH_3CH)$ is about 80 kcal/mol.

If $FeCH_2^+$ from $Fe^+\cdot$propene yields ethylidene as the neutral product, then we can calculate ethylidene's heat of formation by using eq 6, where $E_0(5)$ is the threshold

$$D°_0(CH_2\!\!=\!\!CHCH_3) = E_0(5) + D°_0(Fe^+\!-CH_2) - D°_0(Fe^+\!-C_3H_6) \tag{6a}$$

$$\Delta_f H(CH_3CH) = \Delta_f H(C_3H_6) - \Delta_f H(CH_2) + D°_0(CH_2\!\!=\!\!CHCH_3) \tag{6b}$$

for reaction 5. Unfortunately, as is often the case for small, slowly rising cross sections, it is difficult to obtain a precise value for $E_0(5)$. Our best measurements yield $E_0(5) = 4.96 \pm 0.3$ eV (114 ± 7 kcal/mol). Combined with the literature thermochemistry given in Table II, eq 6 yields $D°_0$-$(CH_2\!\!=\!\!CHCH_3) = 157 \pm 7$ kcal/mol and thus $\Delta_f H$-$(CH_3CH) = 73 \pm 7$ kcal/mol at 0 K. This value for $\Delta_f H$-(CH_3CH) is in reasonable agreement with the two ab initio calculations. The value of $D°_0(CH_2\!\!=\!\!CHCH_3)$ derived here is somewhat smaller than $D°_0(CH_2\!\!=\!\!CH_2)$, 168.9 kcal/mol, but not unreasonably so. Thus, the observed threshold for formation of $FeCH_2^+$ from $Fe^+\cdot$propene is consistent with ethylidene being the neutral product.

CID as a Probe of Structure and Mechanism

While a major goal of the work described in this paper is to determine accurate thermochemistry as discussed above, the $FeC_3H_6^+$ systems also provide an excellent test for the ability of low-energy CID to probe ion structures. Prior CID experiments have provided evidence for the $Fe^+\cdot$propene structure for $FeC_3H_6^+$ produced from propene or propane and the metallacyclobutane for $FeC_3H_6^+$ produced from cyclopropane or cyclobutanone. Peake et al.[6] suggested that the evidence for a metallacyclobutane structure for the latter is not unequivocal based on the high-energy CID results. Since the major product other than direct dissociation is $FeCH_2^+$, the structure could well be $CH_2Fe^+\!-C_2H_4$ rather than the metallacycle. At several

kilovolts, there could even be significant interconversion between the two forms. On the other hand, Jacobson and Freiser[9b] saw no evidence for $CH_2Fe^+\!-C_2H_4$ in their FTMS experiment, and the KERD data of von Koppen et al.[10] indicate a metallacyclic structure as well. It is in cases like this that our ability to do *threshold* CID is most helpful. Since we can observe the products arising from their thresholds at low energy, we can draw conclusions about the structures of the complexes that give rise to them.

Fe⁺·Propene. The differences between the TCA and bimolecular results can give us some insight into both the structure of $Fe^+\cdot$propene and the mechanism of the bimolecular reaction. The most striking difference in the behavior of the two systems is that $FeCH_3^+$ is a major product from reaction of Fe^+ and propene, while it is not seen at all from TCA of $Fe^+\cdot$propene. This discrepancy is easily explained in terms of the $Fe^+\cdot$propene structure consisting of a dative bond between the π electrons of propene and the Fe^+ ion. In this case, collisional activation would be unlikely to lead to $FeCH_3^+$ because the ion would first have to rearrange before the methyl group could become accessible to the Fe^+ ion. On the other hand, in the bimolecular reaction of atomic Fe^+ with propene, the initial orientation of the propene is more random with respect to the ion. An initial interaction with the methyl end of the propene molecule could then lead to production of $FeCH_3^+ + C_2H_3$. The observation that $FeCH_3^+$ is a major product of the bimolecular reaction also implies that Fe^+ reacts with propene much as it does with alkanes,[15,17] in which the weaker bonds tend to be activated preferentially (although at higher energies, stronger bonds can be activated as well).

Metallacycle. The most striking difference in the TCA spectra of $FeC_3H_6^+$ made in the two ways is the much larger amount of $FeCH_2^+$ produced from the cyclopropane adduct than from the propene adduct. The most obvious structures that would produce such a decomposition product are a metallacycle or a $CH_2Fe^+\!-C_2H_4$ structure. $FeCH_2^+$ could easily arise by cleaving across the metallacycle in the former case, or by loss of ethene in the latter. An examination of the threshold behavior enables us to determine which of the two likely structures is most probably the correct one.

The TCA spectrum of $Fe^+\cdot$cyclopropane (Figure 4) shows that $C_3H_5^+$ and $C_3H_6^+$ are both produced. Their production indicates that, at low energy, the ligand is retained as a single moiety since it would take significant rearrangement of a $CH_2Fe^+\!-C_2H_4$ structure to recover these ions as well as the major product, Fe^+. Furthermore, we also observe FeH^+. The thermodynamic threshold for formation of FeH^+ is over 6 eV if the neutral products were either $CH + C_2H_4$ or $CH_2 + C_2H_3$, while the thermodynamic threshold for formation of $FeH^+ + c$-C_3H_5 would be about 2.5 eV (given $D°_0(Fe^+\!-H) = 2.12$ eV[21]). Although determining an exact threshold for FeH^+ is complicated by mass overlap from the much more intense Fe^+ peak, the threshold for its formation is well below 6 eV, implying that it does not arise from decomposition of a presumed $CH_2\!-Fe^+\!-C_2H_4$ ion. While von Koppen et al.[10] point out the possibility that interconversion between the two structures can occur in a single collision, this conclusion from high-energy CID may not be relevant to the present experiment, where there is far less energy available to effect such an interconversion. In any case, our threshold CID strongly suggests that the structure of $FeC_3H_6^+$ created by reaction with cyclopropane or cyclobutanone is a metallacycle.

It is also possible that $Fe^+\cdot$cyclopropane is simply an

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adduct with an intact cyclopropane ring, rather than the metallacycle. Our experiment cannot be conclusive in this regard, and, especially if the barrier to insertion is small, there may not be any real difference between these two structures. The best evidence for a metallacycle rather than an Fe^+·cyclopropane adduct structure is the result from $FeC_3H_6^+$ created by decarbonylation of cyclobutanone. The most reasonable structure for such a product is the metallacycle; since its TCA behavior is indistinguishable from that of the $FeC_3H_6^+$ created by adding cyclopropane to the flow tube, we can infer that the structures are the same.

There are three other conclusions that can be drawn from our observations of Fe^+·cyclopropane. First, if the thermochemistry presented here and our previous paper[11] is correct, then ligand exchange with CO should be exothermic by 0.2 eV. Clearly, from Figure 5, there is a small barrier to ligand exchange, unlike Fe^+·propene, for which the ligand-exchange threshold is consistent with the calculated thermodynamic threshold of 0.14 ± 0.10 eV. One possibility is that there is a barrier to the ligand exchange due to the rearrangement necessary to eliminate C_3H_6 from the metallacycle structure. This seems reasonable as the ligand-exchange reaction in this case actually involves a reductive elimination at the metal center. We have also observed that ligand exchange tends to be less efficient for $Fe(CH_3)_2^+$ than for Fe^+·C_2H_6 due to an isomerization barrier.[12c] Another possibility is that what is observed in this case is not ligand exchange at all, but rather the slightly endothermic reaction to form $FeC_2H_4^+$ and ketene. While we cannot differentiate between $FeC_2H_4^+$ and $FeCO^+$ since they have the same mass, such a complex process, involving cleaving one double bond and forming another, seems unlikely. In any case, it is clear that the $FeC_3H_6^+$ made in our source from reaction with cyclopropane is not Fe^+·propene. This leads to a second conclusion that we can draw, which is that our source conditions do not cause the isomeric forms of $FeC_3H_6^+$ to interconvert, consistent with the arguments by van Koppen et al.[10] for a large interconversion barrier. The direct experimental evidence that we can produce particular isomers will be valuable for future studies of similar complexes.

We can draw a third conclusion from a comparison of the CID experiment with the reaction of Fe^+ with cyclopropane. Since the product distributions are similar, we can conclude that the two reactions are occurring on the same global potential energy surface. This then implies that reaction of Fe^+ with cyclopropane proceeds through a metallacyclic intermediate, as postulated previously for gas-phase transition-metal ions in general.[15,44] The ques-

tion of whether gas-phase atomic transition-metal ions directly activate C–C bonds of unsaturated alkanes has been a subject of some controversy recently,[45] and it is an interesting contrast between straight-chain alkanes in which, apparently, direct C–C bond activation is not necessarily involved at low energy,[46] and cyclopropane, in which it apparently is, both in the gas phase and in the condensed phase.[47,48]

Conclusions

In this paper, we have used low-energy collision-induced dissociation to measure dissociation energies for two isomers of $FeC_3H_6^+$. These values are in good agreement with previous determinations made by a completely different method.[10] We have also measured the bond dissociation energy of Fe^+–CH_2 with greater precision than previous measurements.[15,37] The good agreement between $D°$-(Fe^+–CH_2) measured from the CID experiment and that measured by the reaction of atomic Fe^+ with cyclopropane is evidence that a flow tube source can be reliably expected to produce thermalized polyatomic ions and thereby yield accurate thermochemistry. We also report the first experimental determination of the heat of formation of CH_3CH, ethylidene.

In addition to the thermochemical information we derive from this experiment, we show that low-energy CID can be a useful structural probe of metal–ligand complexes. The probe is effective in two ways: not only from the differences in the thermochemistry of the ions but also from the often considerable differences in the reactivity of different isomers of the same complex. The two isomers of $FeC_3H_6^+$ maintain their structures through the source and reaction regions of our instrument. This observation is particularly significant because it shows that the information gathered from low-energy CID of these complexes ("threshold collisional activation") can be used to obtain information about the mechanisms of the bimolecular reaction of the atomic ion with the free ligand.

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