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# Reactions of Fe$^+$ and Fe(olefin)$^+$ Complexes with Alkenes in the Gas Phase Using Fourier Transform Mass Spectrometry

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**Abstract:** Fourier transform mass spectrometry (FTMS) is used to study the reactions of laser desorbed Fe$^+$ ions with 21 olefins ranging from C$_2$H$_4$ to C$_6$H$_{12}$ isomers. Ethene, propene, and isobutene only undergo a slow condensation reaction with Fe$^+$, while all of the other olefins studied react rapidly with Fe$^+$ eliminating H$_2$, small alkanes, or small olefins generating alkene and alkadiene metal ion products. In addition to primary reactions, secondary, tertiary, and quaternary reactions were studied using swept double resonance ejection techniques. Metal–alkadiene products were observed to abstract carbene from olefins, probably via a metallacyclobutane intermediate, with facile incorporation of the abstracted carbene into the alkadiene framework. With the larger olefins, C–C bond cleavage products dominate the primary reactions while dehydrogenation products are dominant in subsequent reactions. Structures of selected product ions are probed by using collision-induced dissociation (CID). A comparison is made between the CID products of stable Fe(olefin)$^+$ complexes and products resulting from the ion–molecule reactions of Fe$^+$ with the corresponding olefin. Striking differences are observed and discussed.

## Introduction

There have been several recent investigations of the reactions of gas-phase transition metal ions with organic species.[1-5] Generation of olefin–metal ion complexes are the dominant processes observed; however, little is known about the chemistry of these metal ion–olefin complexes. Ridge[4] and Beauchamp[5] have studied the reactions of olefins with Ti$^+$ and Co$^+$, respectively. Dehydrogenation reactions dominated for Ti$^+$ with both dehydrogenation and C–C bond cleavage processes observed for Co$^+$. In those studies, the metal ion was proposed to initially interact with the olefin double bond to form an activated complex which then eliminates hydrogen, small alkanes, or small olefins.

In this study we apply Fourier transform mass spectrometry (FTMS) to study the exothermic reactions of laser-desorbed Fe$^+$ with a variety of olefins. Primary, secondary, tertiary, and quaternary reaction products are observed. Reaction pathways are monitored by using swept double resonance pulses to eject all ions except those of interest and then allowing those ions to react further. Structures of product ions are probed by using collision-induced dissociation (CID).[6-9] In addition, the parent olefin–metal ion complexes are studied by CID and these results are compared and contrasted with those for the corresponding primary reactions.

## Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 mass spectrometer previously described in detail[8,9] and equipped with a 1-in. cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell has been modified by drilling a $^{1}/_{4}$-in. hole in one of the receiver plates permitting irradiation with various light sources. Fe$^+$ was generated by focusing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto the opposite receiver plate which supports a high-purity thin iron foil. Details of the laser ionization experiment have been discussed elsewhere.[2a]

The distribution of product ions listed in Table I are reproducible to within ±10% absolute. Product distributions of subsequent reactions were determined by using swept double resonance ejection techniques[10] to isolate the ions of interest. These ions were then allowed to react further and the products were subsequently detected.

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. Sample pressures were on the order of $1 \times 10^{-7}$ torr. Argon was used as the collision gas at a total pressure of approximately $1 \times 10^{-5}$ torr. A Bayard-Alpert ionization gauge was used to monitor pressure. Details of the CID experiments have previously been discussed.[2d,9] The collision energy of the ions can be varied (typically between 0 and 35 eV) from which plots of CID product ion intensities vs. collision energy can be made. The spread in ion kinetic energies is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.[11] CID can yield unambiguous structural assignments for simple metal ion complexes.[2d,12] Facile rearrangements of complexes containing ligands possessing five or more carbon atoms, however, may yield CID spectra that are not very diagnostic. Therefore, while CID spectra of each major product ion were obtained, many of the structures are necessarily assigned as "reasonable" as opposed to proven.

Finally, in several instances in the text where isomeric neutrals are involved, a generalized equation is used rather than writing separate equations for each isomer. In these cases, unless otherwise indicated, the generalized reaction corresponds to a reactant ion generated from a particular neutral isomer undergoing a subsequent reaction with that same isomer. In the generalized reaction of FeC$_5$H$_8$$^+$ with methylbutene, for example, FeC$_5$H$_8$$^+$ formed from 2-methyl-1-butene was treated with 2-methyl-1-butene, FeC$_5$H$_8$$^+$ formed from 2-methyl-2-butene was treated with 2-methyl-2-butene, and FeC$_5$H$_8$$^+$ formed from 3-methyl-1-butene was treated with 3-methyl-1-butene. No cross reactions, i.e., FeC$_5$H$_8$$^+$ generated from one isomer reacting with another isomer, were investigated.

## Results and Discussion

**Reactions with Ethene, Propene, and Butenes.** No neutral losses were observed in the reactions of ethene, propene, and isobutene with Fe$^+$, with only slow condensation of these olefins onto the metal ions being observed. In contrast to this behavior, linear butenes are readily dehydrogenated by Fe$^+$ to generate a butadiene–metal ion complex. No C–C bond cleavage products are

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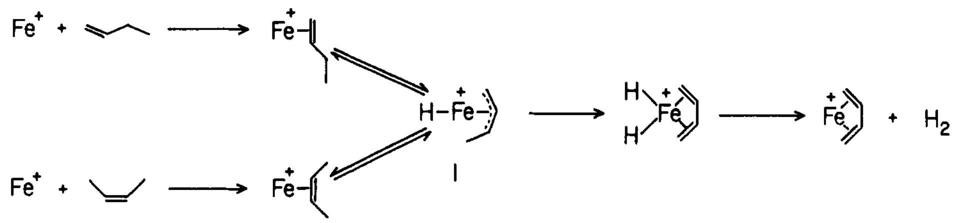
**Table I.** Percentages of Neutral Products Lost in the Primary Reactions of Fe$^+$ with Olefins

| | | neutrals lost | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| alkene | isomer | $H_2$ | $2H_2$ | $CH_4$ | $C_2H_4$ | $C_2H_6$ ($H_2$ + $C_2H_4$) | $C_3H_6$ | $C_3H_8$ ($H_2$ + $C_3H_6$) | $C_4H_8$ | $C_4H_{10}$ |
| $C_4H_8$ | 1-butene | 100 | | | | | | | | |
| | *trans*-2-butene | 100 | | | | | | | | |
| | *cis*-2-butene | 100 | | | | | | | | |
| $C_5H_{10}$ | 1-pentene | 13 | | 19 | 49 | | 19 | | | |
| | *trans*-2-pentene | 19 | | 29 | 30 | | 22 | | | |
| | 2-methyl-1-butene | 26 | | 41 | 28 | | 5 | | | |
| | 3-methyl-1-butene | 21 | | 42 | 29 | | 8 | | | |
| | 2-methyl-2-butene | 35 | | 34 | 24 | | 7 | | | |
| $C_6H_{12}$ | 1-hexene | 10 | | 6 | 14 | 16 | 42 | | 12 | |
| | *trans*-2-hexene | 10 | | 9 | 25 | 22 | 13 | 5 | 12 | 4 |
| | *trans*-3-hexene | 12 | 4 | 14 | 24 | 18 | 10 | 4 | 9 | 5 |
| | 2-methyl-1-pentene | 9 | | 18 | 54 | | 2 | 4 | 11 | 2 |
| | 3-methyl-2-pentene | 14 | | 24 | 23 | 19 | 3 | 4 | 9 | 4 |
| | 4-methyl-1-pentene | 4 | | 22 | 6 | | 56 | 8 | 2 | 2 |
| | 2-methyl-2-pentene | 12 | | 30 | 37 | | 6 | 5 | 6 | 4 |
| | 3,3-dimethyl-1-butene | 10 | | 67 | 10 | | 2 | 6 | 2 | 3 |
| | 2,3-dimethyl-1-butene | 16 | | 62 | 6 | 4 | 2 | 6 | 1 | 3 |
| | 2,3-dimethyl-2-butene | 20 | | 57 | 8 | 4 | | 5 | 4 | 2 |

**Scheme I**



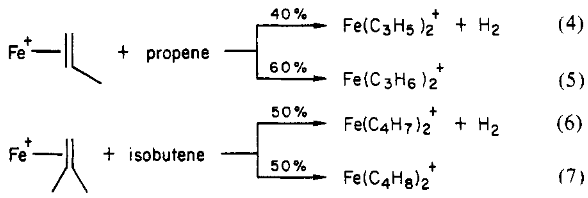
observed for linear butenes. Similarly, Beauchamp[5] reported that only small amounts of C–C bond cleavage products were observed in the reaction of Co$^+$ with linear butenes (about 3% of the total primary product distribution). Dehydrogenation of linear butenes to generate butadiene is a general process observed in the gas-phase chemistry of metal ions[2d,5,12] and is proposed to proceed by the mechanism in Scheme I. Initially, the metal ion generates an activated complex with linear butene which undergoes a facile $\beta$-hydride transfer to the metal generating a hydrido $\pi$-allyl metal complex, **1**. Hydrido $\pi$-allyl metal complexes have been proposed as intermediates in solution-phase chemistry[13-15] and for alkene isomerization and hydrogenation on metal surfaces,[16] and have been implicated in gas-phase metal ion chemistry. Intermediate **1** can undergo a second $\beta$-hydride shift onto the metal resulting in reductive elimination of hydrogen generating a butadiene–metal ion complex.[17] The dehydrogenation process was further investigated by studying the reaction of Fe$^+$ with 1-butene-*1,1-d*$_2$. Although loss of $H_2$ dominated, substantial amounts of HD elimination along with some $D_2$ loss were also observed (reactions 1–3). These results suggest that the hydrido $\pi$-allyl complex, **1**, is in rapid equilibrium with the metal ion–butene complex[18] as shown in Scheme I.

$$\mathrm{Fe^+} + \text{1-butene-}\mathit{1,1\text{-}d}_2 \xrightarrow{65\%} \mathrm{FeC_4H_4D_2^+} + \mathrm{H_2} \quad (1)$$

$$\xrightarrow{32\%} \mathrm{FeC_4H_5D^+} + \mathrm{HD} \quad (2)$$

$$\xrightarrow{3\%} \mathrm{FeC_4H_6^+} + \mathrm{D_2} \quad (3)$$

The absence of neutral losses in reactions with ethene and propene indicates that dehydrogenation to form ethyne, propyne, or allene is an unfavorable process. The absence of any neutral losses for reaction with isobutene indicates that dehydrogenation to form a trimethylene methane complex or rearrangements involving metallacyclobutanes is also unfavorable.



A much richer chemistry is observed for the Fe(olefin)$^+$ species than for Fe$^+$. Reactions 4–7 are observed for Fe(propene)$^+$ and Fe(isobutene)$^+$, respectively. The products in reactions 4 and 6 probably consist simply of bis(allyl)–metal ion complexes. More complicated species may be present, however, where dehydrogenation has been centered on one olefin or where the two olefins have coupled to eliminate hydrogen. Observation of significant amounts of the condensation products in reactions 5 and 7 suggest that dehydrogenation generating bis(allyl) complexes may be near thermoneutral. The overall process of converting two propenes or two isobutenes to the corresponding allyl species and $H_2$ requires 71 and 67 kcal/mol, respectively.[19] Observation of reaction 4, therefore, requires $D°(\mathrm{Fe^+(C_3H_5)–C_3H_5}) + D°(\mathrm{Fe^+–C_3H_5})$ −

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(17) No distinction will be made between the syn and anti (shown) forms of the 1-methylallyl species, since their interconversion via a 1-butene complex is possible. However, it seems reasonable to speculate that the dehydrogenation probably occurs primarily via the anti isomer.

(18) Reversible $\beta$-hydride transfers have been observed in gas-phase metal ion chemistry. See, for example, ref 1d, 3b, 3f, and Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445.

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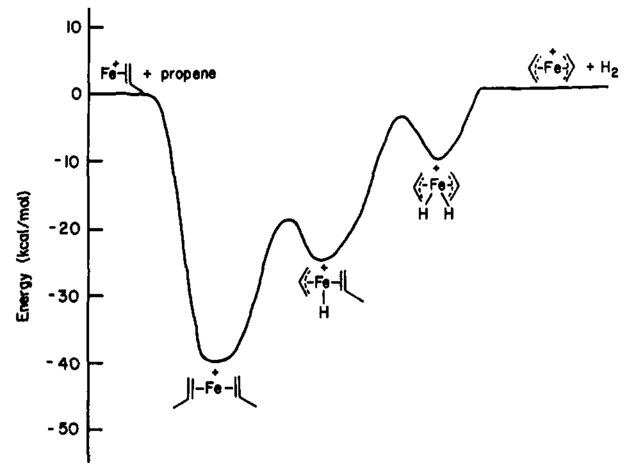
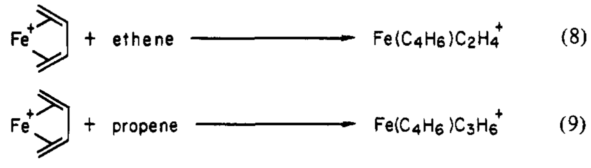
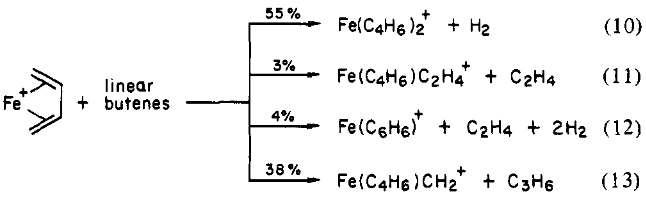


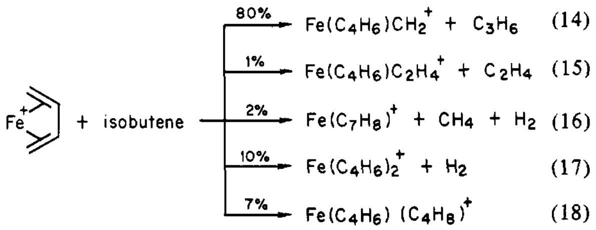
**Figure 1.** Potential energy diagram for dehydrogenation of propene by Fe(propene)$^+$ generating bis(allyl)Fe$^+$.

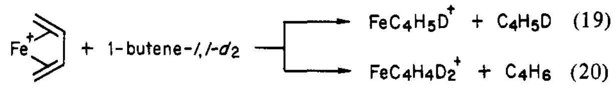
$D^\circ$(Fe$^+$–propene) > 71 kcal/mol to be exothermic (assuming allyl products). Beauchamp et al. have recently determined that $D^\circ$(Co$^+$–ethene) = 37 ± 2 kcal/mol.[3e] Using similar arguments, we have also assigned $D^\circ$(Fe$^+$–ethene) = 37 kcal/mol.[20] Larger olefins are found to be somewhat more strongly bound to metal ion centers than smaller olefins.[2d,12,21] Assuming $D^\circ$(Fe$^+$–propene) ~ 40 kcal/mol, then $D^\circ(\text{Fe}^+(\text{C}_3\text{H}_5)\text{–C}_3\text{H}_5) + D^\circ(\text{Fe}^+\text{–C}_3\text{H}_5)$ must be greater than 111 kcal/mol for reaction 4 to occur. Assuming reaction 4 is thermoneutral implies $D^\circ(\text{Fe}^+(\text{C}_3\text{H}_5)\text{–C}_3\text{H}_5) + D^\circ(\text{Fe}^+\text{–C}_3\text{H}_5) = 111$ kcal/mol yielding an average for $D^\circ(\text{Fe}^+\text{–C}_3\text{H}_5) = 55.5$ kcal/mol. Using the values $D^\circ$(Fe$^+$–propene) = 40 kcal/mol, $D^\circ(\text{Fe}^+\text{–C}_3\text{H}_5) = 55$ kcal/mol, $D^\circ$(Fe$^+$–H) = 58 kcal/mol,[3d] and assuming that the above bond energies do not change when another ligand is added to the metal (H, propene, or allyl), then a qualitative potential energy diagram for the reaction of Fe(propene)$^+$ with propene can be drawn (Figure 1). Initially, propene coordinates to Fe(propene)$^+$ producing a complex activated by about 40 kcal/mol internal energy. This is followed by a $\beta$-hydride shift onto the metal forming a $\pi$-allyl–hydrido complex which consumes 15 kcal/mol internal energy. A second $\beta$-hydride shift onto the metal produces a dihydride–bis(allyl) complex. This process again is endothermic by roughly 15 kcal/mol. Finally, dehydrogenation occurs generating the bis(allyl)–Fe$^+$. Hence, all the intermediates leading to formation of the bis(allyl) complex in this scheme are energetically accessible.

Ethene and propene react with Fe(butadiene)$^+$ to produce exclusively the condensation products in reactions 8 and 9, respectively. Structural studies indicate that the products of reactions 8 and 9 consist simply of Fe(butadiene)–alkene$^+$ complexes. Significant amounts of C–C bond cleavage products are observed in reactions of Fe(butadiene)$^+$ with linear butenes and isobutene, reactions 10–18, and demonstrate that the presence of a diene bound to Fe$^+$ can have profound effects on the chemistry. The results for isobutene are particularly surprising in light of the propene results in reaction 9. The rate of reaction for the linear butenes with Fe(butadiene)$^+$ is approximately one-fifth that for reactions of linear butenes with Fe$^+$. Fe(butadiene)$^+$ reacts with 1-butene-*1,1*-$d_2$ to initially produce labeled butadiene bound to Fe$^+$, reactions 19 and 20, with reaction 19 dominating over reaction 20. Ultimately, the products of reactions 19 and 20 generate products analogous to those seen in reactions 10–13, with varying degrees of deuteration. Formation of labeled Fe(butadiene)$^+$ indicates that several reversible $\beta$-hydride transfers occur in the collision complex prior to dehydrogenation. A mechanism for reaction of 1-butene with Fe(butadiene)$^+$ is illustrated in Scheme II. Initially, the collision complex, **2**, undergoes a $\beta$-hydride shift generating **3**, a 15-electron complex. Several reversible hydride shifts can now occur as shown in Scheme II. The net effect is scrambling of the hydrogens. Regeneration of the initial collision complex, **2**, with the hydrogens scrambled, can simply undergo loss of butene-forming reactants. A second $\beta$-hydride shift can occur producing **4**, a 17-electron complex, which reductively eliminates hydrogen generating presumably bis(butadiene)Fe$^+$, reaction 10.

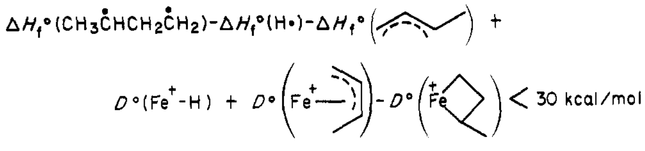








The C–C bond cleavage processes, reactions 11 and 13, may proceed through a metallacyclobutane intermediate, **5**, as shown in Scheme II. The initial collision complex, **2**, is activated by the butene–metal ion bond strength (approximately 40 kcal/mol). Using the bond energies discussed earlier for reaction 4, formation of intermediate **3** consumes 10 kcal/mol, leaving it with 30-kcal/mol excess internal energy. For formation of **5**, the metallacyclobutane, to be exothermic requires the process



to be less than 30 kcal/mol endothermic (the amount of excess internal energy in complex **3**). Using $\Delta H_f^\circ(\text{CH}_3\dot{\text{C}}\text{HCH}_2\dot{\text{C}}\text{H}_2) = 59$ kcal/mol,[19] then formation of **5** requires the bond strength of $\text{CH}_3\dot{\text{C}}\text{HCH}_2\dot{\text{C}}\text{H}_2$ to Fe$^+$ to be >60 kcal/mol for the overall process to be exothermic. $D^\circ(\text{Fe}^+\text{–CH}_3) = 69 \pm 5$ kcal/mol;[3f] hence, formation of **5** appears to be energetically accessible, even if there is considerable strain energy associated with the metallacyclobutane. The metallacyclobutane can then decompose yielding the corresponding carbene species (olefin metathesis) resulting in elimination of $\text{C}_3\text{H}_6$ or $\text{C}_2\text{H}_4$[22-27] with $\text{C}_3\text{H}_6$ loss dominating over $\text{C}_2\text{H}_4$ loss. Formation of the carbene species, (butadiene)FeCH$_2^+$, in reaction 13 is approximately thermoneutral[19] using $D^\circ(\text{Fe}^+\text{–CH}_2) = 96 \pm 5$ kcal/mol.[3d] Carbene

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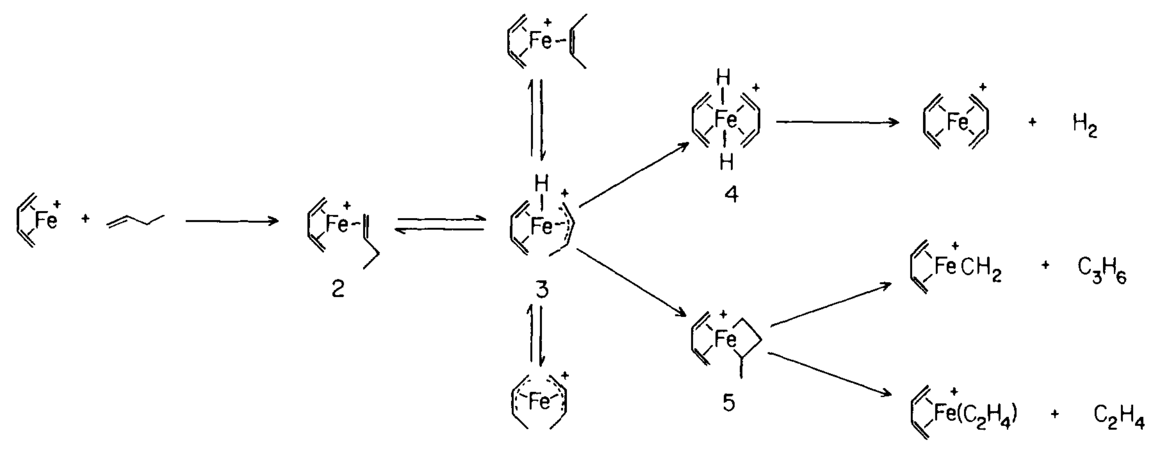
Scheme II



abstraction with isobutene, reaction 14, can be viewed similarly. The dominance of carbene abstraction vs. dehydrogenation in the reaction of isobutene with Fe(butadiene)$^+$ is a manifestation of the difficulty for Fe$^+$ to dehydrogenate isobutene. Absence of carbene abstraction for propene by Fe(butadiene)$^+$ may be due to the inaccessibility of high-energy intermediates leading to carbene abstraction since the overall process is roughly thermoneutral as for the butenes discussed above.

The absence of any C–C bond cleavage products for reaction of linear butenes with Fe$^+$ indicates that formation of a metallacyclobutane intermediate by reversible hydride transfers is not competitive with dehydrogenation. However, formation of metallacyclobutane intermediates may become competitive with dehydrogenation for reactions of linear butenes with Fe(butadiene)$^+$. The factors responsible for this are not well understood. However, it may be due to the effects of the butadiene ligand on Fe$^+$ to open up new reaction channels or simply that the rapid reversible $\beta$-hydride shifts allow for formation of metallacyclobutanes to be competitive with dehydrogenation (a kinetic effect).

The structure of the dehydrogenation product in reaction 10 was probed both by specific ion–molecule reactions and by CID. Acetonitrile sequentially displaces $C_4H_6$ from $Fe(C_4H_6)_2^+$, reaction 21. This is strong evidence for formation of bis(butadiene)Fe$^+$

$$\mathrm{Fe(C_4H_6)_2^+ \xrightarrow{CH_3CN} Fe(C_4H_6)CH_3CN^+ \xrightarrow{CH_3CN} Fe(CH_3CN)_2^+} \quad (21)$$

in reaction 10. Benzene readily displaces butadiene from Fe(butadiene)$^+$; however, the bis(butadiene)Fe$^+$ species is unreactive with benzene. The inert behavior of bis(butadiene)Fe$^+$ toward benzene may be due to a lack of sufficient empty sites available for benzene coordination prior to displacement.

The variation of CID product ion intensities as a function of collision energy for $Fe(C_4H_6)_2^+$ generated in reaction 10 is shown in Figure 2. Generation of $FeC_4H_6^+$ and $FeC_6H_6^+$ are the only CID products observed. Simple cleavage yields $FeC_4H_6^+$; however, considerable rearrangement is required to obtain $FeC_6H_6^+$. Formation of $FeC_6H_6^+$ may proceed via an initial metal-assisted Diels–Alder cycloaddition generating a 4-vinylcyclohexene–metal ion complex. This is followed by reversible $\beta$-hydride shifts resulting in loss of $C_2H_4$ and $H_2$ producing Fe(benzene)$^+$. No loss of $2H_2$ generating Fe(styrene)$^+$ is observed. The $FeC_6H_6^+$ observed in reaction 12 may, therefore, be generated by initial dehydrogenation to generate a bis(butadiene)–metal ion species, reaction 10, which can undergo the above cycloaddition process to generate Fe(benzene)$^+$ provided it retains sufficient internal energy. This process for Fe(benzene)$^+$ formation in reaction 12 requires $D°$(Fe$^+$–benzene) to be 6 kcal/mol greater than $D°$(Fe$^+$–butadiene) to be exothermic.

Both acetonitrile and benzene displace exclusively $C_5H_8$ from $FeC_5H_8^+$ produced in reactions 13 and 14. Neither benzene nor acetonitrile displaces $CH_2$ from $FeCH_2^+$. In addition, $C_2H_2$, $C_2H_4$, and $C_3H_6$ are the only CID products observed for the $FeC_5H_8^+$ ions generated in reactions 13 and 14. The absence of displacement of $C_4H_6$ by acetonitrile and benzene or $C_4H_6$ loss in the CID spectra suggests that the abstracted carbene has become incorporated into the butadiene framework. The CID results are similar to those obtained for both Fe(methylbutadiene)$^+$ and Fe(pentadiene)$^+$ species. Conversions of butadiene–iron–carbene to either Fe(methylbutadiene)$^+$ or Fe(pentadiene)$^+$ are both exothermic by roughly 5 kcal/mol[19] assuming equal bonding of the alkadienes to Fe$^+$.

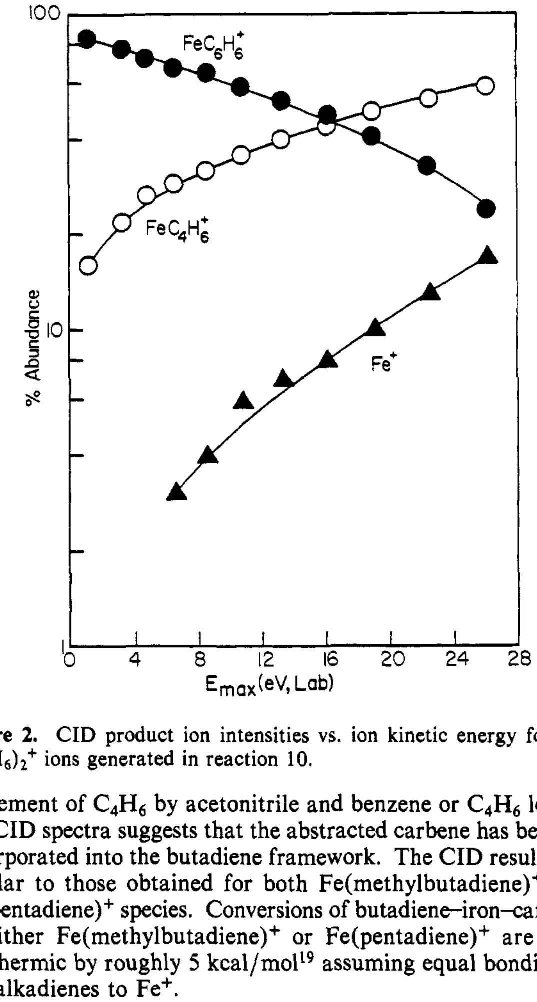
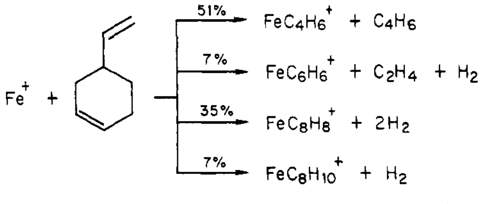


**Figure 2.** CID product ion intensities vs. ion kinetic energy for $Fe(C_4H_6)_2^+$ ions generated in reaction 10.

The reactions of Fe$^+$ with 4-vinylcyclohexene were studied in order to probe the above cycloaddition mechanism for formation of $Fe(C_6H_6)^+$ (reaction 12). Four products were observed (reactions 22–25). In addition, these primary products react with



(22)

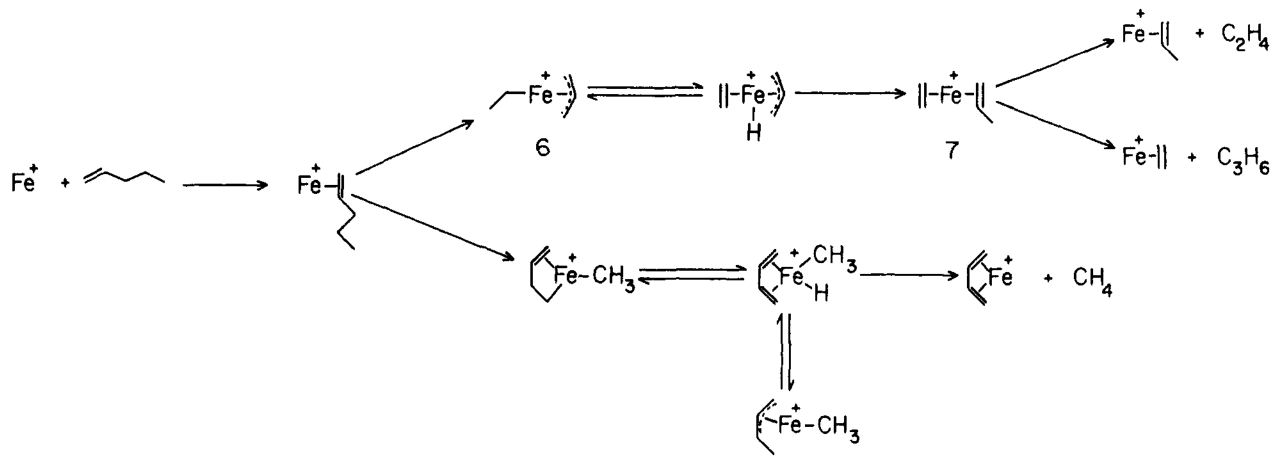
(23)

(24)

(25)

a second 4-vinylcyclohexene to generate $FeC_8H_{12}^+$ (ligand displacement) as the only product. CID of this product yields formation of $FeC_6H_6^+$ as the dominant fragment. The only other fragmentation was loss of $C_4H_6$ generating $FeC_4H_6^+$. These results

Scheme III



provide further evidence for the Diels–Alder cycloaddition mechanism proposed above for formation of $\mathrm{Fe(C_6H_6)^+}$. The product of reaction 16 may consist of a toluene–metal ion complex generated via the cycloaddition reaction described above. In this case cycloaddition would produce a 4,4-dimethylcyclohexene intermediate which could eliminate $\mathrm{CH_4}$ and $\mathrm{H_2}$ generating the toluene complex.

The product of reaction 13, $\mathrm{FeC_5H_8^+}$, is observed to react with linear butenes to generate two products, $\mathrm{Fe(C_9H_{14})^+}$ and $\mathrm{Fe(C_6H_{10})^+}$. The former product may be produced simply by two successive $\beta$-hydride shifts onto the metal resulting in reductive elimination of hydrogen as in reaction 10. $\mathrm{FeC_6H_{10}^+}$ may be produced in a manner analogous to that for $\mathrm{FeC_5H_8^+}$ in reaction 13.

**Reactions with Linear Pentenes.** The neutral losses for the primary reactions of $\mathrm{Fe^+}$ with 1-pentene and *trans*-2-pentene are shown in Table I. Both C–C bond cleavage and dehydrogenation products are observed in the primary reactions, in contrast to linear butenes where only dehydrogenation is observed. A mechanism for C–C bond cleavage is presented in Scheme III for 1-pentene. The initial step in this mechanism involves oxidative addition of an allylic C–C bond generating an alkyl $\pi$-allyl complex, **6**, or oxidative addition of a terminal C–C bond. This is followed by $\beta$-hydride shifts resulting in generation of a bisolefin complex, **7**, in the former and reductive elimination of $\mathrm{CH_4}$ producing a butadiene complex in the latter. The bisolefin complex can then eliminate either of the olefins. Loss of $\mathrm{C_2H_4}$ dominates over loss of $\mathrm{C_3H_6}$ (Table I) which is consistent with larger olefins being more strongly bound to metal ion centers than smaller olefins.[2d,12,21] Hence, smaller olefins will be preferentially cleaved from bis(olefin) complexes. Loss of $\mathrm{C_2H_4}$ and $\mathrm{C_3H_6}$ by *trans*-2-pentene probably involves prior isomerization to 1-pentene by reversible $\beta$-hydride shifts. An alternative possibility exists for the loss of $\mathrm{CH_4}$ in the 1-pentene system where prior isomerization to 2-pentene occurs. Insertion into an allylic C–C bond would then result in generation of a butadiene–metal ion complex. Alternatively, the C–C bond cleavage process may proceed through metallacyclobutane intermediates; however, it appears that this process would not be nearly as facile as that described above.

Conversion of linear pentenes to propene and ethene requires 9 kcal/mol more energy than conversion to butadiene and methane.[19] In addition, butadiene will be bound more strongly to the metal center than an alkene;[3c,21] hence, insertion into the terminal C–C bond of linear pentenes produces thermally more stable products than insertion into an internal C–C bond. The small fraction of terminal C–C bond insertion (Table I) indicates that either a high-energy intermediate is involved or the frequency factor for insertion into the allylic C–C bond of 1-pentene is much higher than that for the terminal C–C bond of 2-pentene. Oxidative addition into allylic C–C bonds of olefins smaller than linear pentene would generate intermediates having no labile $\beta$ hydrogens; hence, C–C bond cleavages are not expected and not observed for linear butenes. The small fraction of dehydrogenation of linear pentenes (Table I) indicates that insertion into C–C bonds is considerably more facile than C–H bond insertion for activated (linear pentene)–$\mathrm{Fe^+}$ complexes.

The secondary reactions for both 1-pentene and *trans*-2-pentene are strikingly similar. Only simple ligand displacement reactions are observed for smaller olefins bound to $\mathrm{Fe^+}$. Pentene, for example, is observed to simply displace $\mathrm{C_2H_4}$ and $\mathrm{C_3H_6}$ to generate $\mathrm{FeC_5H_{10}^+}$. Secondary reactions of alkadiene–metal ion complexes become more complicated where simple olefin displacement is not possible. Three products are observed in the reactions of $\mathrm{FeC_4H_6^+}$ with pentene (reactions 26–28). Generation of $\mathrm{FeC_5H_8^+}$ (reaction 26) is by far the dominant process (>90%) and may be formed by several processes. As demonstrated in the butene reactions described above, the dominant process probably consists simply of two successive $\beta$-hydride transfers from pentene to butadiene generating a butene–pentadiene complex with subsequent loss of butene. In addition, $\mathrm{CH_2}$ may be abstracted from pentene generating a butadiene–carbene–metal ion complex as in Scheme II. The former process should be more facile than the latter. Formation of $\mathrm{FeC_6H_{10}^+}$ (reaction 27) can also be envisioned as proceeding through a process similar to Scheme II where the carbene species may come from either the butadiene ligand or pentene. Only a trace of dehydrogenation is observed probably producing a (butadiene)(pentadiene)–$\mathrm{Fe^+}$ species.

$$\mathrm{FeC_4H_6^+ + pentene \longrightarrow FeC_5H_8^+ + C_4H_8} \qquad (26)$$

$$\mathrm{FeC_4H_6^+ + pentene \longrightarrow FeC_6H_{10}^+ + C_3H_6} \qquad (27)$$

$$\mathrm{FeC_4H_6^+ + pentene \longrightarrow Fe(C_5H_8)(C_4H_6)^+ + H_2} \qquad (28)$$

Although the chemistry observed for $\mathrm{FeC_5H_8^+}$ (reactions 29–32) is similar to that of $\mathrm{FeC_4H_6^+}$ described above, the product distributions are vastly different. Here, dehydrogenations are the dominant processes producing $\mathrm{Fe(C_5H_8)_2^+}$ and $\mathrm{Fe(C_{10}H_{14})^+}$ in roughly equal amounts. Two other products, $\mathrm{FeC_6H_{10}^+}$ and $\mathrm{FeC_7H_{12}^+}$, could be generated via Scheme II producing carbene species. Generation of $\mathrm{FeC_7H_{12}^+}$ from 1-pentene would require prior isomerization to 2-pentene which can then form a symmetrical metallacyclobutane, **9**. This can then rearrange to the corresponding carbene eliminating propene.

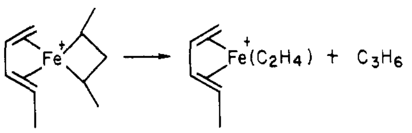
$$\mathrm{FeC_5H_8^+ + pentene \longrightarrow Fe(C_6H_{10})^+ + C_4H_8} \qquad (29)$$

$$\mathrm{FeC_5H_8^+ + pentene \longrightarrow Fe(C_7H_{12})^+ + C_3H_6} \qquad (30)$$

$$\mathrm{FeC_5H_8^+ + pentene \longrightarrow Fe(C_5H_8)_2^+ + H_2} \qquad (31)$$

$$\mathrm{FeC_5H_8^+ + pentene \longrightarrow Fe(C_{10}H_{14})^+ + 2H_2} \qquad (32)$$

Reactions of $\mathrm{FeC_5H_{10}^+}$ (pentene attachment) are simple and involve dehydrogenations or C–C bond cleavages (loss of $\mathrm{C_2H_4}$ or $\mathrm{C_3H_6}$). No loss of $\mathrm{CH_4}$, generating $\mathrm{FeC_9H_{16}^+}$, was observed



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for either pentene. Carbon bond cleavage reactions dominated for 1-pentene whereas dehydrogenation products dominated for 2-pentene. This indicates that 2-pentene probably isomerizes to 1-pentene before C–C bond cleavages are observed. $Fe(C_5H_{10})(C_2H_4)^+$ and $Fe(C_5H_{10}{}^+)(C_3H_6)^+$ react with pentene by simple olefin displacement to generate $Fe(C_5H_{10})_2{}^+$ species.

**Reactions with Linear Hexenes.** The primary product distributions (Table I) for the reactions of $Fe^+$ with three linear hexenes are similar, indicating that some degree of isomerization probably occurs prior to elimination of a neutral species. The primary products can be envisioned as being generated by processes outlined in Scheme III. CID of the $FeC_4H_8{}^+$ ions produced from all three hexenes is consistent with the generation of linear butene complexes, as predicted in Scheme III. The formation of $FeC_4H_6{}^+$ (a butadiene complex) deserves further comment. This ion may be formed by either loss of $C_2H_6$ (ethane) or by loss of $C_2H_4$ followed by dehydrogenation. Loss of ethane from the hexenes requires that $D°(Fe^+–C_4H_6) > 19$ kcal/mol to be exothermic, and loss of $C_2H_4 + H_2$ requires $D°(Fe^+–C_4H_6) > 52$ kcal/mol.[19] Bond energies of 1,3-alkadienes are in the range 45–60 kcal/mol for $Co^+$ [5] with $Fe^+$ probably lying within this range. Hence, $FeC_4H_6{}^+$ is believed to be formed predominantly by loss of ethane since loss of $C_2H_4 + H_2$ would be near thermoneutral.

Only one product is observed in the reaction of $FeC_4H_6{}^+$ with the hexenes, formation of $FeC_6H_{10}{}^+$, in contrast to the results for linear butenes and linear pentenes discussed earlier. This product is probably formed via two successive β-hydride shifts from hexene to butadiene to generate a hexadiene–butene complex that loses butene, similar to the process discussed for linear butenes.

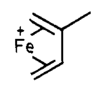
Surprisingly, four products are observed in the reactions of $FeC_5H_8{}^+$ with linear hexenes (reactions 33–36). The dominant

$$FeC_5H_8{}^+ + \text{hexene} \rightarrow FeC_6H_{10}{}^+ + C_5H_{10} \quad (33)$$
$$\rightarrow Fe(C_5H_8)(C_3H_6)^+ + C_3H_6 \quad (34)$$
$$\rightarrow Fe(C_6H_{10})(C_5H_8)^+ + H_2 \quad (35)$$
$$\rightarrow Fe(C_{11}H_{16})^+ + 2H_2 \quad (36)$$

process is generation of $FeC_6H_{10}{}^+$ which probably occurs via two successive β-hydride transfers as described earlier. The dehydrogenation products, $Fe(C_{11}H_{16})^+$ and $Fe(C_6H_{10})(C_5H_8)^+$, simply proceed by β-hydride shifts resulting in reductive elimination of hydrogen. The absence of the corresponding dehydrogenation products for $FeC_4H_6{}^+$ may be due to the increased steric bulk of the pentadiene ligand which may allow reductive elimination of hydrogen to become competitive with β-hydride transfers resulting in loss of pentene. Only dehydrogenation products are observed for reactions of $FeC_6H_{10}{}^+$ with linear hexenes producing $Fe(C_6H_{10})_2{}^+$ and $Fe(C_6H_{10})(C_6H_8)^+$ in roughly equal amounts.

The chemistry of $FeC_6H_{12}{}^+$ for 1-hexene is considerably different from that of either *trans*-2-hexene or *trans*-3-hexene. Reaction with 1-hexene yields predominantly loss of $C_3H_6$ to generate $Fe(C_6H_{12})(C_3H_6)^+$, probably via facile insertion into the allylic C–C bond as in Scheme III. The only other processes seen are dehydrogenations. Reaction of the corresponding $FeC_6H_{12}{}^+$ with *trans*-2-hexene or *trans*-3-hexene generates two C–C bond cleavage products, $Fe(C_6H_{12})(C_2H_4)^+$ and $Fe(C_6H_{12})(C_4H_8)^+$, with no $Fe(C_6H_{12})(C_3H_6)^+$ being produced. In addition, dehydrogenation products are also observed.

**Reactions with Methylbutenes.** Reactions of $Fe^+$ with the three methylbutenes (2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene) are all similar (Table I). Both C–C bond cleavage and dehydrogenation products are observed in the primary reactions in contrast to linear butenes where only dehydrogenation is observed. The generation of significant C–C bond cleavage products indicates that isomerization of the olefin skeleton by $Fe^+$ may be quite facile. Dehydrogenation may simply generate an isoprene species **10** or the corresponding substituted tri-



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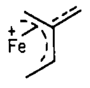


11

methylenemethane complex **11**. Methane loss could generate either butadiene or a trimethylenemethane species. Experiments involving specific reactivity or CID failed to distinguish between these two structures. Furthermore, rearrangement of **11** to **10** by β-hydride shifts is possible.

The secondary reactions of the $FeC_4H_6{}^+$ ions generates three products (reactions 37–39), with formation of $FeC_5H_8{}^+$ domi-

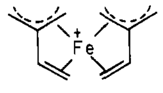
$$FeC_4H_6{}^+ + \text{methylbutene} \rightarrow FeC_5H_8{}^+ + C_4H_8 \quad (37)$$
$$\rightarrow Fe(C_4H_6)(C_5H_8)^+ + H_2 \quad (38)$$
$$\rightarrow Fe(C_9H_{12})^+ + 2H_2 \quad (39)$$

nating. This product is probably formed predominantly by sequential β-hydride shifts to butadiene resulting in loss of butene. A small amount may be generated by Scheme II producing a carbene species. Dehydrogenations are the only other products observed. Loss of $H_2$ may generate a butadiene–methylbutadiene complex. Loss of $2H_2$ may generate a species in which the two ligands have been coupled.

Three products are generated in reactions of $FeC_5H_8{}^+$ with methylbutenes (reactions 40–42). Dehydrogenations are the

$$FeC_5H_8{}^+ + \text{methylbutene} \rightarrow Fe(C_6H_{10})^+ + C_4H_8 \quad (40)$$
$$\rightarrow Fe(C_5H_8)_2{}^+ + H_2 \quad (41)$$
$$\rightarrow Fe(C_{10}H_{14})^+ + 2H_2 \quad (42)$$

dominant processes with loss of $H_2$ and $2H_2$ occurring about equally. The product of reaction 42 may simply consist of a bis(allylpropene) structure **12**, or the two ligands may have

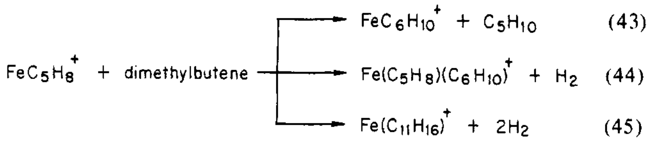


12

coupled. The generation of $FeC_6H_{10}{}^+$ (reaction 40) may proceed through a metallacyclic intermediate generating a carbene species. $FeC_5H_{10}{}^+$, generated by displacement of $C_2H_4$ or $C_3H_6$, yields three products upon reaction with the appropriate methylbutene. Dehydrogenations are dominant with some loss of $C_3H_6$ occurring generating $Fe(C_5H_8)(C_2H_4)^+$ ions.

**Reactions with Dimethylbutenes.** As with the methylbutenes described above, C–C bond cleavages dominate over dehydrogenation products in the primary reactions of dimethylbutenes (Table I). Several products are observed with loss of $CH_4$ being by far the dominant process (>50%) generating $FeC_5H_8{}^+$. CID can readily distinguish between different $FeC_4H_8{}^+$ structures and is used here for that purpose. The CID results indicate that the $FeC_4H_8{}^+$ generated from 3,3-dimethyl-1-butene consists of an isobutene–metal ion complex. Fragmentations from CID of $FeC_4H_8{}^+$ produced in reactions with 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene, however, are consistent with formation of linear butene–metal ion complexes.

The secondary reactions are similar to those observed for the methylbutenes previously discussed. $FeC_4H_8{}^+$ reacts by simple ligand displacement to produce $FeC_6H_{12}{}^+$. $FeC_5H_8{}^+$ reacts further to generate three products (reactions 43–45). Formation of $FeC_6H_{10}{}^+$ (reaction 43) is the dominant process, probably being generated by successive β-hydride shifts across the metal resulting in elimination of $C_5H_{10}$. The only other products observed are

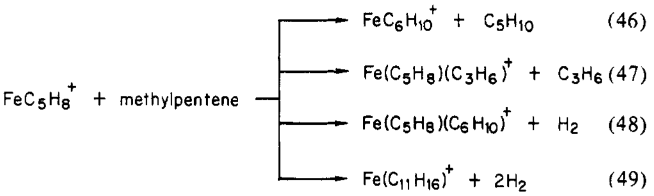


$$\mathrm{FeC_5H_8^+} + \text{dimethylbutene} \rightarrow \mathrm{FeC_6H_{10}^+ + C_5H_{10}} \tag{43}$$
$$\rightarrow \mathrm{Fe(C_5H_8)(C_6H_{10})^+ + H_2} \tag{44}$$
$$\rightarrow \mathrm{Fe(C_{11}H_{16})^+ + 2H_2} \tag{45}$$

dehydrogenations, reactions 44 and 45, with a 2:1 ratio of $2H_2$ vs. $H_2$ loss. Only two dehydrogenation products are seen in the reactions of $FeC_6H_{10}^+$ generating $FeC_{12}H_{18}^+$ and $FeC_{12}H_{20}^+$ in roughly equal amounts. The ion intensity of $FeC_6H_{12}^+$ (direct attachment) was too low to allow it to be studied.

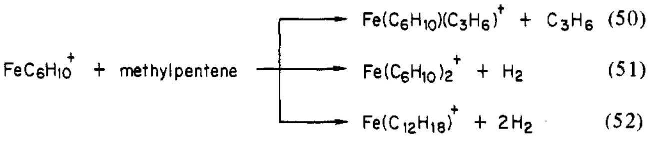
**Reactions with Methylpentenes.** The neutral losses for the primary reactions with several methylpentenes are presented in Table I. There are significant differences in the primary product distributions for the different methylpentenes, in contrast to the other olefin isomers. The differences can easily be correlated to the different olefin structures by mechanisms previously outlined. Again, the structures of the $FeC_4H_8^+$ ions can be probed by CID. These CID results indicate that 3-methyl-1-pentene produces an $FeC_4H_8^+$ complex consisting of a linear butene with the other three olefins generating $FeC_4H_8^+$ species consisting of isobutene units bound to $Fe^+$. These results are all in accord with those which are expected except for 4-methyl-1-pentene where isomerization may be necessary before loss of $C_2H_4$ can occur.

The secondary reactions are similar for all four methylpentenes studied. Again, small olefins bound to $Fe^+$ yield simple displacements to generate $FeC_6H_{12}^+$. Four different products are observed for $FeC_5H_8^+$, reactions 46–49. Formation of $FeC_6H_{10}^+$ is the dominant process as expected from previous results. The other three products occur in smaller amounts in roughly equal quantities (each about 8% of the total product distribution). The product of reaction 47 is interesting in that it occurs for all four olefins, even when only very minor amounts of $FeC_3H_6^+$ are seen for their primary reactions.



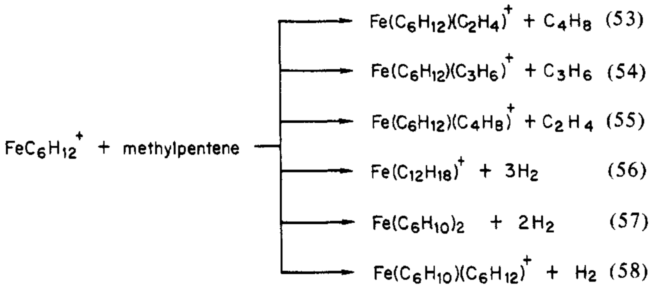
$$\mathrm{FeC_5H_8^+} + \text{methylpentene} \rightarrow \mathrm{FeC_6H_{10}^+ + C_5H_{10}} \tag{46}$$
$$\rightarrow \mathrm{Fe(C_5H_8)(C_3H_6)^+ + C_3H_6} \tag{47}$$
$$\rightarrow \mathrm{Fe(C_5H_8)(C_6H_{10})^+ + H_2} \tag{48}$$
$$\rightarrow \mathrm{Fe(C_{11}H_{16})^+ + 2H_2} \tag{49}$$

Three products are observed in the reactions of $FeC_6H_{10}^+$ with 4-methyl-1-pentene (reactions 50–52), with only two products (reactions 51 and 52) being observed for the other methylpentenes. Loss of $2H_2$ dominates over loss of $H_2$ by a 2:1 ratio in all cases. Loss of $C_3H_6$ for 4-methyl-1-pentene accounts for about 20% of the product distribution and indicates that insertion into the allylic C–C bond is facile as evidenced by the primary reaction product distributions.



$$\mathrm{FeC_6H_{10}^+} + \text{methylpentene} \rightarrow \mathrm{Fe(C_6H_{10})(C_3H_6)^+ + C_3H_6} \tag{50}$$
$$\rightarrow \mathrm{Fe(C_6H_{10})_2^+ + H_2} \tag{51}$$
$$\rightarrow \mathrm{Fe(C_{12}H_{18})^+ + 2H_2} \tag{52}$$

$FeC_6H_{12}^+$ ions react to yield six different products (reactions 53–58). Reaction 54 is unique to 4-methyl-1-pentene whereas reactions 53 and 55 occur for all the methylpentenes except 4-methyl-1-pentene. Reactions 56–58 are observed for all four methylpentenes. Reaction 54 is by far the dominant process (about 75%) for 4-methyl-1-pentene and probably proceeds through initial insertion into the allylic C–C bond. Loss of $C_2H_4$ dominates over loss of $C_4H_8$ by a 2:1 ratio. Loss of $2H_2$ is about twice as intense as either loss of $3H_2$ or $H_2$. The products of reactions 53–55 are observed to react with another methylpentene by simple displacement generating $Fe(C_6H_{12})_2^+$ species.



$$\mathrm{FeC_6H_{12}^+} + \text{methylpentene} \rightarrow \mathrm{Fe(C_6H_{12})(C_2H_4)^+ + C_4H_8} \tag{53}$$
$$\rightarrow \mathrm{Fe(C_6H_{12})(C_3H_6)^+ + C_3H_6} \tag{54}$$
$$\rightarrow \mathrm{Fe(C_6H_{12})(C_4H_8)^+ + C_2H_4} \tag{55}$$
$$\rightarrow \mathrm{Fe(C_{12}H_{18})^+ + 3H_2} \tag{56}$$
$$\rightarrow \mathrm{Fe(C_6H_{10})_2 + 2H_2} \tag{57}$$
$$\rightarrow \mathrm{Fe(C_6H_{10})(C_6H_{12})^+ + H_2} \tag{58}$$

**Comparison of CID with Ion–Molecule Reactions.** The CID product distributions for stable Fe(olefin)$^+$ complexes can be compared with the results for the primary reaction product distributions (Table II). The initial complex formed in an $Fe^+$–olefin collision is activated with 40–60 kcal/mol excess internal energy[3f] which results in the elimination of a smaller neutral fragment. CID of stable Fe(olefin)$^+$ complexes should yield similar results to those for the primary reactions when their internal energies are comparable. The maximum amount of internal energy that can be obtained by an ion in a single collision event is given by eq 59 where $E_0$ is the internal energy, $m_1$ is the mass of the target,

$$E_0 = (m_1/(m_1 + m_2))K_0 \tag{59}$$

$m_2$ is the mass of the ion, and $K_0$ is the kinetic energy of the ion.[28] Hence, the maximum internal energy obtained by $FeC_6H_{12}^+$ is $0.222K_0$ and for $FeC_5H_{10}^+$ is $0.241K_0$ for a single collision with argon as the target.

CID efficiencies are very low for single collision conditions, even at high ion kinetic energies. Under multiple collision conditions, however, the CID efficiencies increase dramatically. In addition, the thresholds for observing fragmentation is much lower under multiple collision conditions. Hence, the fragmentations observed here are in large part the result of multiple collisions.[29] This indicates that most collisions impart considerably less than the maximum internal energy to the ion. The maximum internal energy obtained by an ion allowed to undergo, to the limit, an infinite number of collisions is given by eq 60, where $U_{max}$ is the

$$U_{max} = [(m_1 + m_2)/(2m_2 + m_1)]K_0 \tag{60}$$

maximum internal energy.[29] Since most of the energy is acquired by the ion in the first few collisions, eq 60 should be satisfied (only at threshold) under experimental conditions where several collisions are occurring.

A plot of the distribution of ion intensities vs. collision energy for CID of stable Fe(3,3-dimethyl-1-butene)$^+$ complex is shown in Figure 3. The CID product distributions are considerably different from those for the primary reactions at all energies. Table II lists the distributions of neutral losses observed by CID of several stable Fe(olefin)$^+$ complexes accelerated to ~8 eV kinetic energy.

Several major differences are seen between the CID and ion–molecule results. These differences are most prominent for branched olefins. One possible explanation for these differences is that the stable Fe(olefin)$^+$ species (generated by displacement of a smaller olefin) has isomerized to a structure different from that of the displacing olefin prior to analysis by CID. This seems unlikely since the overall reaction is probably less than 2 kcal/mol exothermic.[21]

A more likely explanation may lie in the nature of the two methods. As discussed above, the conditions for CID are such that multiple collisions are occurring prior to fragmentation. Each individual collision will impart internal energy into the ion. The net effect is that the ions gain internal energy in a stepwise manner. Several metal assisted rearrangements may then be sampled before the ion has gained sufficient internal energy for fragmentation to occur. These low-energy rearrangements would be expected to be more facile for branched olefins than for linear olefins. This is exactly what is seen in Table II.

In the ion–molecule reactions, the collision complex gains a fixed amount of energy in a single event which allows for more direct losses to compete with the low-energy rearrangements.

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**Table II.** Percentages of Neutral Losses from CID of $Fe(olefin)^+$ Complexes Accelerated to 8 eV Kinetic Energy[a,b]

| | | neutrals lost | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| alkene | isomers | $H_2$ | $CH_4$ | $C_2H_4$ | $C_2H_6$ ($H_2$ + $C_2H_4$) | $C_3H_6$ | $C_3H_8$ ($H_2$ + $C_3H_6$) | $C_4H_8$ | $C_4H_{10}$ |
| $C_5H_{10}$ | 1-pentene | | 4 | 87 | | 9 | | | |
| | *trans*-2-pentene | | 9 | 79 | | 12 | | | |
| | 2-methyl-1-butene | | 10 | 80 | | 10 | | | |
| | 3-methyl-1-butene | | 11 | 80 | | 9 | | | |
| | 2-methyl-2-butene | 4 | 11 | 71 | 3 | 11 | | | |
| $C_6H_{12}$ | 1-hexene | | | 17 | 10 | 73 | | | |
| | *trans*-2-hexene | | 3 | 52 | 37 | 4 | 1 | 3 | |
| | *trans*-3-hexene | | 4 | 52 | 34 | 5 | 3 | 2 | |
| | 2-methyl-1-pentene | | 4 | 91 | | 2 | | 2 | 1 |
| | 3-methyl-1-pentene | | 9 | 55 | 30 | 3 | | 3 | |
| | 4-methyl-1-pentene | | | 5 | 1 | 88 | 6 | | |
| | 2-methyl-2-pentene | | 5 | 87 | | 5 | | 3 | |
| | 2,3-dimethyl-1-butene | | 27 | 48 | 18 | 3 | | 2 | 2 |
| | 3,3-dimethyl-1-butene | | 5 | 88 | | 4 | | 3 | |
| | 2,3-dimethyl-2-butene | | 32 | 46 | 19 | | 1 | 1 | 1 |

[a] Argon used as target at ~1 × $10^{-5}$ torr. [b] CID interaction time of 25 ms.

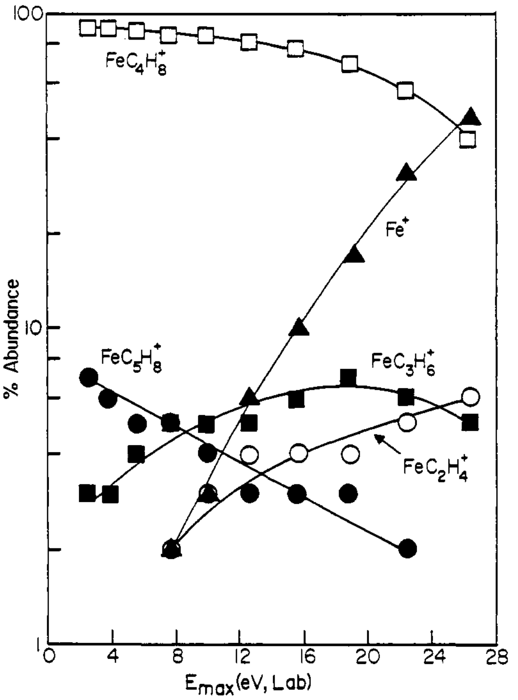

**Figure 3.** CID product ion intensities vs. ion kinetic energy for Fe(3,3-dimethyl-1-butene)$^+$.

## Conclusions

The primary reactions of olefins with $Fe^+$ yield results similar to those previously reported for $Co^+$.[5] Primary reactions are dominated by C–C bond cleavage processes for alkenes larger than butene with dehydrogenations dominating for subsequent reactions. Products of reactions with linear olefins are easily explained by processes similar to Scheme III. Many products obtained from branched olefins, however, are not easily explained and may arise through metallacyclobutane intermediates. Ethene, propene, and isobutene gave no neutral losses when reacted with $Fe^+$, with only slow condensation of the olefin on the metal ion being observed. The lack of dehydrogenation for isobutene by $Fe^+$ indicates that formation of a trimethylene methane complex is unfavorable.

A much richer chemistry is observed in the reactions of Fe(alkadiene)$^+$ with olefins than $Fe^+$. These differences are readily demonstrated in the reactions of Fe(butadiene)$^+$ with butenes (reactions 10–18). These results may simply be attributed to the effects a butadiene ligand has on $Fe^+$ to open up new reaction channels or simply that rapid reversible β-hydride shifts allow for formation of metallacyclobutane intermediates to become competitive with dehydrogenation (a kinetic effect). Carbene abstraction from olefins by Fe(alkadiene)$^+$, presumably occurring via a metallacyclobutane intermediate, readily occurs. Incorporation of carbene into the alkadiene framework is facile as evidenced by both ligand exchange and CID results.

Several differences are seen in CID of stable Fe(olefin)$^+$ complexes vs. products from reactions of $Fe^+$ with the corresponding olefin. These differences are most significant for branched olefins. These differences may be attributed to the nature of the two processes. In the CID experiment, the ion complex gains internal energy in a stepwise fashion through multiple collisions allowing metal-assisted rearrangements to occur. In the ion–molecule reactions, the collision complex gains a fixed amount of internal energy in a single collision event which permits more direct losses to dominate over rearrangements. This hypothesis will be tested by studying CID in a triple quadrupole under single collision conditions and by photodissociation.

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