gives rise to k_{slow} in polymerized **1** vesicles. A similar situation has been encountered in the dithionite ion cleavage of 5,5'-dithiobis(2-nitrobenzoic acid), Ellman's reagent, in dihexadecyl-dimethylammonium vesicles.[26] The relative contributions of the fast and slow components of the reaction varied as a function of time elapsed (46 ms to 1–5 s) between the addition of the Ellman's reagent and the dithionite ion. These results were rationalized in terms of the time required for distribution of the substrate between the vesicle surface (k_{fast}) and substrate (k_{slow}).[26]

Observation of the three reaction sites in polymerized **1** vesicles does not imply an identical behavior in nonpolymerized vesicles. Clearly, reactivities in vesicles and polymerized vesicles are complex and their understanding presents a worthy challenge.

Structural Characterization of Gas-Phase Complexes of Alkanes, Alkenes, and Carbon Monoxide with the Atomic Iron Ion

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Abstract: Gas-phase clusters of Fe^+ with hydrocarbons and carbon monoxide are characterized by collision-induced decomposition (CID) mass spectrometry. The clusters are formed in ion–molecule reactions of $Fe(CO)_n^+$ ions with hydrocarbons and ketones. Two different $FeC_4H_{10}^+$ species are characterized. $FeC_3H_8^+$, $FeC_2H_6^+$, and $FeCH_4^+$ species are observed and characterized. Oxidative addition of C–C and C–H bonds to the metal occurs in these complexes. Four different $FeC_4H_8^+$ species are characterized. $FeC_4H_6^+$ formed in four different reactions are all found to have the same structures, a metal–1,3-butadiene complex. $FeC_3H_6^+$ and $FeC_2H_4^+$ species formed in several different reactions are found to be metal–olefin complexes. Four different species of stoichiometry $FeCOC_4H_{10}^+$ are observed. Evidence of $FeCO^+$ insertion into C–C and C–H bonds in these species is described. Two different $FeCOC_2H_6^+$ species are observed. Two different FeH_2CO^+ species are observed, one of which has the hydrogen atoms bound to the metal. Evidence is presented that addition of C–H bonds to the metal occurs in $Fe_2(CO)_4C_4H_{10}^+$ clusters. Correlation is observed between the CID spectra of several ions and the exothermicity of the reactions in which they are formed. Product distributions for reaction between butanes and Fe^+ formed by 70-eV electron impact on $Fe(CO)_5$ matches product distributions obtained for Fe^+ formed in other ways. It is deduced from the CID spectrum of one isomer of $FeCOC_2H_6^+$ that $IP(FeCH_3) \approx IP(CH_3CO)$, which implies $D(Fe-CH_3) \approx 42$ kcal/mol.

The first examples of oxidative addition of alkane carbon–carbon bonds to transition metals have recently been reported.[1-3] Evaporated clusters of Ni atoms[1] and Zr atoms,[2] for example, when condensed with alkanes react to form smaller alkanes. The group 8 first-row atomic ions react in the gas phase with alkanes to form smaller alkanes and metal–olefin complexes.[3,4] The discovery of gas-phase oxidative addition processes involving carbon–carbon bonds provides a unique opportunity to study the dynamics of oxidative addition. Important thermochemical and mechanistic information on the formation of metal to carbon bonds has been obtained in several such studies.[3-14]

We recently described the formation of complexes of alkanes with atomic transition-metal ions.[4] The complexes result from ion–molecule reactions in metal carbonyls and are stable in the gas phase. These complexes might be considered the simplest case of an alkane absorbed on a metal surface. The initial communication described the structural characterization of complexes of Fe^+ with the C_4H_{10} isomers using the techniques of collision-induced-dissociation mass spectrometry.[4] The present report describes more complete characterization of complexes of Fe^+ with 2-methylpropane and butane as well as characterization of Fe^+ complexes with propane, ethane, and methane. Metal–olefin complexes formed in the reactions of Fe^+ with the alkanes are also characterized.

The effects of adding a CO ligand to a metal–alkane complex are probed by examining the collision-induced decomposition spectra of $FeCO(C_4H_{10})^+$, $FeCO(C_2H_6)^+$, and FeH_2CO^+ ions prepared in several ways. Ions of the $Fe_2(CO)_4(C_4H_{10})^+$ stoichiometry are structurally examined to probe the effect of an additional Fe atom in the cluster.

Experimental Section

The collision-induced decomposition experiments were performed on a three-sector mass spectrometer at the Midwest Center for Mass Spectrometry. The instrument, described in detail elsewhere,[15] is a

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Table I. Fragmentation Patterns of Complexes of C_4H_{10} Isomers with Fe+

fragments	branching ratios for Fe+ + n-C_4H_{10} reaction				branching ratios for Fe+ + (CH$_3$)$_3$CH reactions			
	collision-induced dissociation of Fe(C_4H_{10})+ [a]	Fe+ from electron impact on Fe(CO)$_5$ [a,b]	Fe+ from laser desorption [c]	Fe+ from thermionic emission [d]	collision-induced dissociation of Fe(CH$_3$)$_3$CH+ [a]	Fe+ from electron impact on Fe(CO)$_5$ [a,b]	Fe+ from laser desorption [c]	Fe+ from thermionic emission [d]
FeC$_4$H$_8$+	0.11	0.12 (0.06[b])	0.12	0.27	0.38	0.41 (0.16[b])	0.38	0.54
FeC$_4$H$_7$+	0.02				0.02			
FeC$_4$H$_6$+	0.04	0.06 (0.09[b])	e	0.07				
FeC$_3$H$_6$+	0.19	0.32 (0.10[b])	0.29	0.36	0.32	0.59 (0.84[b])	0.62	0.46
FeC$_2$H$_4$+	0.20	0.51 (0.75[b])	0.59	0.28				
FeCH$_3$+	0.07				0.05			
FeH+	0.10				0.03			
Fe+	0.27				0.20			

[a] Present results. [b] Branching ratios for the deuterated butanes, C_4D_{10}, from ref 4. [c] From ref 6. [d] From ref 5. [e] May be present in a small amount. Mass ambiguity and signal-to-noise problems prevent precise determination.

Kratos MS50 TA with a second electrostatic analyzer following the normal mass filter of the MS50. In this study the first two sectors mass selected (resolution >5000) the ions of interest before the ions entered a collision chamber in the third field-free region. Helium was used as the collision gas and was introduced until there was 50% suppression of the primary beam. The third-sector mass analyzed the collision fragments. The spectra were acquired by computer and signal averaged. The reproducibility of the relative intensities of the peaks in the CID spectra was determined by comparing spectra taken at different times during the course of this study. The maximum variation in peak intensities between runs was ±2% of the total intensity of the fragment ion peaks with the exceptions noted in the tables.
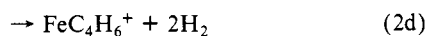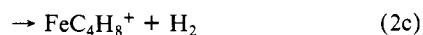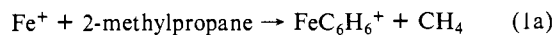
In some instances metastable decompositions were observed in the absence of collision gas. They were always much less intense than the decompositions observed in the presence of collision gas. Peak intensities observed in the presence of collision gas was therefore taken to represent the results of collision-induced decompositions.

All experiments were conducted using a chemical ionization (high pressure) source as 6-kV accelerating voltage and at source temperatures less than 100 °C (heater off). The electron ionizing energy was 70 eV. The total pressure of the source was not measured directly, but the source housing was in the 10^{-5}–10^{-4} torr range, suggesting source pressures of several tenths of a torr. Most of the source pressures was hydrocarbon gas. The lesser part (from one-tenth to one-third) was iron pentacarbonyl.

All samples were obtained through commercial sources. No impurities were observed in the mass spectra of the samples.

Results and Discussions

Reactions of Fe+ with Butanes. Fe+ undergoes reactions 1 and 2 with the butanes.[3–6] Table I notes the product ratios obtained

$$Fe^+ + 2\text{-methylpropane} \rightarrow FeC_6H_6^+ + CH_4 \quad (1a)$$

$$\rightarrow FeC_4H_8^+ + H_2 \quad (1b)$$

$$Fe^+ + \text{butane} \rightarrow FeC_2H_4^+ + C_2H_6 \quad (2a)$$

$$\rightarrow FeC_3H_6^+ + CH_4 \quad (2b)$$

$$\rightarrow FeC_4H_8^+ + H_2 \quad (2c)$$

$$\rightarrow FeC_4H_6^+ + 2H_2 \quad (2d)$$

in several studies. Product ratios for reaction of Fe+ from electron impact on Fe(CO)$_5$ were first determined by ion cyclotron resonance techniques.[3,4] In the present study these product distributions were determined from the high-resolution mass spectra of mixtures of Fe(CO)$_5$ with the butanes. These spectra were obtained with the MS-50TA under the same source conditions used to obtain the CID spectra discussed below. Recently the reactions of alkanes with Fe+ produced thermionically[5] and Fe+ produced by laser desorption from a solid iron surface[6] have been described. The product distributions in these two studies are also given in Table I. The agreement between the product distributions obtained by the three methods is quite good. The present results and the laser desorption results agree within combined experimental uncertainties. The original ion cyclotron resonance (ICR) product distributions (the numbers in parentheses in the table)

were obtained by using butanes-d_{10} which may have resulted in an isotope effect. The d-10 isobutane-d_{10} loses D_2 to a lesser extent than the undeuterated isobutane loses H_2. This is the expected isotope effect, if the mechanisms discussed below are correct. The relative abundances of the various product channels observed with ions produced thermionically are somewhat different from those observed in the present study and the laser desorption study, particularly in the case of the relative abundances of channels 2a and 2c. It should be noted, however, that the thermionic results are for ions with 1 eV of translational energy in the center of mass relative to the neutral reactant. The translational energy dependence of reactions of Co+ analogous to reactions 1 and 2 has been determined.[7] In the reaction of Co+ the ratio of (2a) to (2c) decreases with translational energy from thermal energy to 1 eV.[7] A similar effect for the Fe+ reaction may account for the discrepancy between the thermionic result and the other two results. It is possible that the Fe+ ions are formed in a distribution of electronic states by electron impact on Fe(CO)$_5$ or by laser desorption from the metal surface. The agreement between the various product distributions in Table I indicates either that each method produces Fe+ in approximately the same distribution of states or that all the states of Fe+ produced react in approximately the same way. The simplest and most probable explanation is that all three methods produce predominantly the ground state of Fe+ and that none of the methods produce any Fe+ in states with chemistry significantly different from that of the ground state.

Formation of (Hydrocarbon)iron(+). Reaction 3 occurs in mixtures of Fe(CO)+ and an alkane. The Fe(CO)+ reactant is formed by electron impact on Fe(CO)$_5$. The ionic products of

$$Fe(CO)^+ + \text{alkane} \rightarrow (\text{alkane})\text{iron}(+) + CO \quad (3)$$
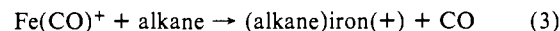
reaction 3 where the alkane is a butane are lower energy variants of the collision complexes that decompose to products in reactions 1 and 2. The product of reaction 3 is stable and can be further examined to elucidate the mechanisms of the reactions 1 and 2. This is a unique opportunity, since the product of (3) represents the simplest case of an alkane absorbed onto a metal surface. Collision-induced decomposition (CID) mass spectrometry is the technique used in this study to characterize the (alkane)iron(+) species.

Principles for Interpretation of CID Spectra. In this experiment, ions are prepared in the ion source and mass filtered. The ions are then excited by high-energy (6 kV) collisions with helium gas, and a mass spectrum of the resulting decomposition products is obtained. Information about ion structures is inferred from these CID spectra in two different ways. First, the structure of an ion can be deduced from the fragmentation processes observed in the CID spectrum in the same way that neutral molecular structures are deduced from fragmentation observed in mass spectra. Second, the CID spectrum of an ion of unknown structure can be used as a "fingerprint" and compared to the CID spectrum of an ion of known structure. If the two match, then the two ions are assumed to have the same structure. There are difficulties with both methods. Assumptions must be made about the dynamics
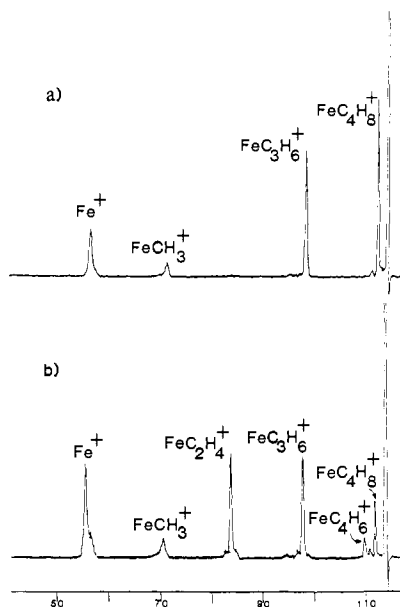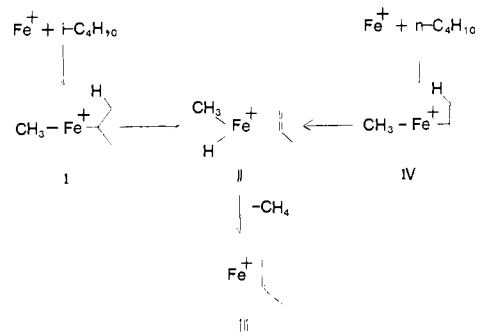
Figure 1. The collision-induced decomposition spectra of $Fe(C_4H_{10})^+$ (m/z 114) formed in the ion source by reaction of $FeCO^+$ with 2-methylpropane (a) and butane (b).

of the decomposition process in order to relate the fragmentation pattern to structure. It is assumed in most of the interpretations discussed below that simple bond cleavage sometimes accompanied by some motion of an H atom is much more probable than complex nuclear rearrangements.[16] The problem with using CID spectra as structural "fingerprints" is that identical CID spectra are necessary but not sufficient to establish structural identity. In addition, ions with essentially the same structure but different energy content could give somewhat different CID spectra. Therefore, identification of a structure requires careful consideration of all the information available about an ion in addition to its CID spectrum. For that reason ion–molecule reactions and thermochemical information are sometimes considered in discussing the CID spectra and ion structures.
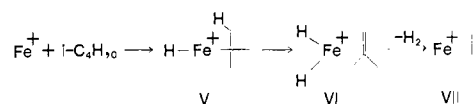
To minimize variability associated with different degrees of internal excitation care was taken to assure that ions to be compared were prepared at nearly the same conditions of temperature, pressure, electron-beam energy, etc. In several cases it was possible to prepare the same ion by using several reactions of different exothermicity. The ions formed in the different reactions have CID spectra that differ somewhat from one another. Ions formed in the more exothermic reactions tend to show slightly more intense peaks for the higher energy decomposition products in their CID spectra. These results help to evaluate the role of internal energy in determining the CID spectrum of the various ions.

$FeC_4H_{10}^+$. The CID spectra in Figure 1 are those of the $FeC_4H_{10}^+$ species formed in reaction 3 where the hydrocarbon is 2-methylpropane (Figure 1a) or butane (Figure 1b). The relative intensity of the collision fragments in the spectra are summarized in Table I. The spectra in Figure 1 agree quite well with those reported in our initial communication.[4] The present spectra have a better signal to noise ratio as a result of signal averaging. One important feature immediately evident from the data in Table I is that the products of reaction 1 appear as major collision fragments of the $FeC_4H_{10}^+$ ion made from 2-methylpropane by reaction 3. In addition, the products of reaction 2 appear as major collision fragments of the $FeC_4H_{10}^+$ ion made from butane by reaction 3. This indicates that the reactions of Fe^+ with the butanes occur on the same potential surface as the
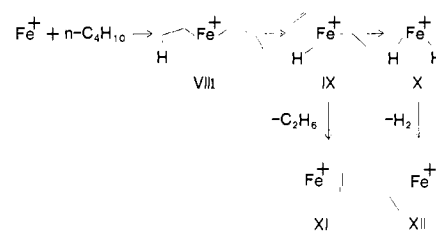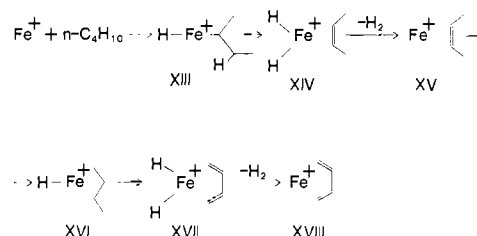
(16) The energy deposited in a polyatomic ion in a 6-kV collision with a He atom is 1–10 eV and the distribution is broad (see: Kim, S. M.; McLafferty, F. W. *J. Am. Chem. Soc.* **1978**, *100*, 3279-3282). The average ion will thus have energy well in excess of that required for several decomposition pathways. Under these circumstances, the pathways requiring the least motion prevail.

Scheme I

Scheme II

Scheme III

Scheme IV

CID of the $FeC_4H_{10}^+$ complexes. A second striking feature of the two CID spectra is that $FeC_2H_4^+$ is a very important ion in the spectrum of the $FeC_4H_{10}^+$ complex made from butane (Figure 1b) but is completely absent from the spectrum of the $FeC_4H_{10}^+$ complex made from 2-methylpropane (Figure 1a). This establishes that the two $FeC_4H_{10}^+$ ions do, indeed, assume different structures. It also suggests that complicated rearrangements of the carbon skeleton do not occur in the complex either before or after collisional excitation. A third feature of the two spectra is that the Fe^+ fragment is only about one-fourth of the total fragment ion intensity. This emphasizes the strong interaction between the metal ion and the butanes. It supports the notion that covalent bonds are formed in the metal–butane complexes.

The specific decomposition pathways of the $FeC_4H_{10}^+$ complexes are readily rationalized in terms of structures thought to be intermediates to reactions 1 and 2. Mechanisms for these reactions are outlined in Schemes I–IV. All of the proposed mechanisms share the essential features of that shown for reactions 1a in Scheme I. One of the bonds of the hydrocarbon adds oxidatively to the metal, forming a species such as I. A hydrogen atom from the β carbon is transferred to the metal, forming an alkyl metal hydride with an olefin ligand such as II. Reductive elimination of an alkane or H_2 gives a metal–olefin complex such as III. A scheme of this kind resulting in elimination of CH_4 from butane (reaction 2b) is also given in Scheme I. A mechanism for elimination of H_2 from 2-methylpropane (reaction 1b) is given in Scheme II. Mechanisms for reactions 2a and 2c of n-butane are given in Scheme III. An alternative mechanism for (2c) (relative to that in Scheme III) and a mechanism for reaction 2d

Gas-Phase Complexes of Fe⁺

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Table II. CID Spectra of FeC₄H₈⁺ Isomers from Ion-Molecule Reactions[a]

	reactants						
fragments	Fe⁺ + (CH₃)₃CH	Fe(CO)⁺ + (CH₃)₂CCH₂	Fe(CO)⁺ + 2-C₄H₈[b]	Fe⁺ + n-C₄H₁₀	Fe⁺ + ⬠=O	Fe(CO)₂⁺ + 2(C₂H₄)	33% 2(C₂H₄) + 67% (C₄H₈)
FeC₄H₇⁺	0.06	0.02	0.03	0.03	0.02	0.02	0.03
FeC₄H₆⁺	0.02	0.01	0.72	0.46	0.45		0.48
FeC₃H₄⁺	0.11	0.12		0.007			
FeC₃H₃⁺	0.05	0.04	0.007	0.01	0.01		0.01
FeC₂H₄⁺			0.007	0.20	0.30	0.62	0.21
FeC₂H₃⁺	0.02	0.02	0.03	0.05	0.05	0.10	0.05
FeCH₃⁺	0.12	0.09	0.01	0.02	0.02		0.01
FeH⁺	0.05	0.04	0.03	0.02		0.05	0.03
Fe⁺	0.52	0.62	0.15	0.15	0.15	0.15	0.15

[a] Relative intensities normalized by setting the total of the fragment ion intensities equal to 1. [b] The FeC₄H₈⁺ ions from 1-C₄H₈ and 2-C₄H₈ gave identical spectra.

of *n*-butane are given in Scheme IV.

The major fragments in the CID spectrum of the complex of Fe⁺ with 2-methylpropane (Figure 1a) are FeC₄H₈⁺ and FeC₃H₆⁺. These form as a result of reductive elimination of H₂ and CH₄ from VI and II, respectively. These reductive eliminations involve only slightly more nuclear motion than a simple bond cleavage. Minor fragments include FeCH₃⁺ and FeH⁺, which could result from single-bond cleavages in I and V, respectively. The low-energy pathway to an FeCH₃⁺ fragment involves cleavage of I into FeCH₃⁺ and 2-propyl radical. In such a process the 2-propyl radical could compete with the FeCH₃⁺ for the charge. The absence of a C₃H₇⁺ fragment from the spectrum suggests that IP(FeCH₃) < IP(2-propyl radical) ≈ 7.36 eV.[17] This is consistent with the FeCH₃ ionization potential determined from the FeC₃H₆O⁺ CID discussed below. The FeC₄H₁₀⁺ ion formed by reaction of FeCO⁺ with 2-methylpropane is thus suggested to be predominantly a mixture of structures II and VI. Lesser amounts of I and V may also be present. The Fe⁺ peak results from either the loss of intact 2-methylpropane from a loosely bound ion-induced dipole complex or the stepwise loss of smaller fragments from structures such as II and VI.

The formation of structures such as I and II in the reaction of FeCO⁺ with 2-methylpropane (reaction 3) indicates that these structures are not high-energy transition states but low-energy configurations of the complex of Fe⁺ with 2-methylpropane. This complex has as much as 63 kcal/mol (=D(Fe⁺–CO)[18]) less energy than that formed in the direct reaction of Fe⁺ with 2-methylpropane. Still, structures such as I and II are formed. This implies that the potential surface on which reaction 1 occurs is characterized by a well without large barriers on the pathways between reactants and products.

Besides Fe⁺, the major fragments in the CID spectrum of the complex of Fe⁺ with butane are FeC₂H₄⁺ and FeC₃H₆⁺. These fragments are readily formed on collisional excitation of structure IX and structure II (see Schemes III and I), respectively. The less abundant FeC₄H₈⁺ fragment results from either X or XIV. FeCH₃⁺ and FeH⁺ are formed from structures IV and XIII (Schemes I and IV), respectively, as a result of simple bond cleavage processes. The FeC₄H₇⁺ and FeC₄H₆⁺ fragments are a collisionally excited species originally of structure XIV that loses H and H₂ or 2H₂ as outlined in Scheme IV. This involves rearrangement of H atoms after the collision but not reorganization of the carbon skeleton.

The potential surface for reaction 2, like that for reaction 1, is characterized by a well without large barriers between reactants and products. Structures such as IX and X represent a minima in the paths leading to the various reactants. The complex of Fe⁺ with butane formed in the reaction of FeCO⁺ with butane assumes structures IX and II a large proportion of the time. Other structures such as XIII and XIV also play a role.

(17) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067–74.

(18) Based on heats of formation of Fe(CO)ₙ⁺ ions: Distefano, G. *J. Res. Nat. Bur. Stand., Sect. A* **1970**, *74A*, 233.
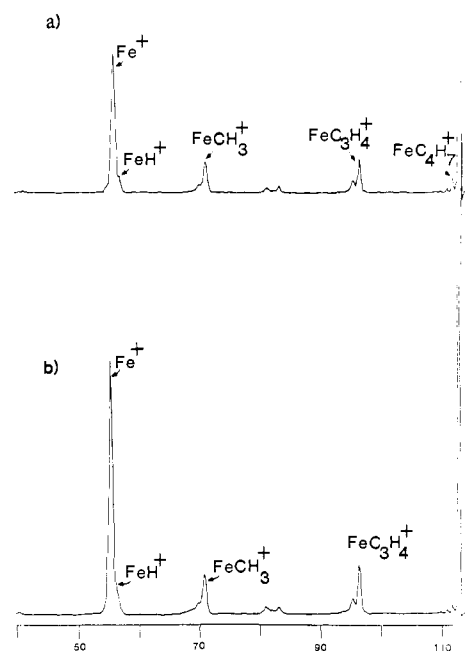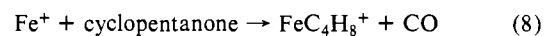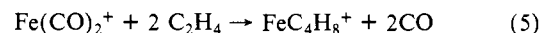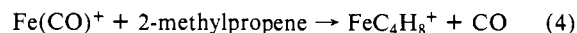

Figure 2. The collision-induced decomposition spectra of Fe-[(CH₃)₂CCH₂]⁺ (*m/z* 112) formed in the ion source by reaction 1b between Fe⁺ and 2-methylpropane (a) and reaction 4 of FeCO⁺ and 2-methylpropene (b).

It is difficult to assess the relative importance of the two possible mechanisms for reaction 2c given in Schemes III and IV. The formation of FeC₄H₆⁺ in reaction 2d indicates that the mechanism in Scheme IV plays some role. It would be useful, in this connection, to know the structure of the product of reaction 2c. In fact, all of the proposed mechanisms of reaction 1 and 2 give specific structures for the products. Verification of the observed product structures would therefore be useful in evaluating the proposed mechanisms. Considered next are CID experiments designed to characterize the structures of the products of reaction 1 and 2.

FeC₄H₈⁺. The CID spectra for the FeC₄H₈⁺ complexes formed in reactions 1b, 2c, and 4–8 are shown in Figures 2 and 3. The

$$Fe(CO)^+ + 2\text{-methylpropene} \rightarrow FeC_4H_8^+ + CO \quad (4)$$

$$Fe(CO)_2^+ + 2\ C_2H_4 \rightarrow FeC_4H_8^+ + 2CO \quad (5)$$

$$FeCO^+ + 1\text{-}C_4H_8 \rightarrow FeC_4H_8^+ + CO \quad (6)$$

$$FeCO^+ + 2\text{-}C_4H_8 \rightarrow FeC_4H_8^+ + CO \quad (7)$$

$$Fe^+ + \text{cyclopentanone} \rightarrow FeC_4H_8^+ + CO \quad (8)$$

relative intensities for these spectra are in Table II. The CID

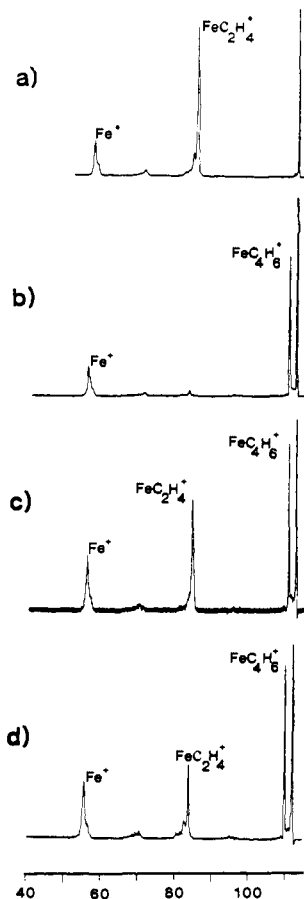**Figure 3.** The collision-induced decomposition spectra of $Fe(C_4H_8)^+$ (m/z 112) formed in the ion source by reaction 5 between $Fe(CO)_2^+$ and ethylene (a), reaction 7 between $FeCO^+$ and 2-butene (b) (the spectra for the product of reaction of $FeCO^+$ and 1-butene is identical with that shown in b), reaction 8 between Fe^+ and cyclopentanone (c), and reaction 2c between Fe^+ and butane (d).

Figure 4. The collision-induced decomposition spectra of $Fe(C_4H_6)^+$ (m/z 110) formed in the ion source by reaction 11 between Fe^+ and 1-butene (a), reaction 12 between Fe^+ and 2-butene (b), reaction 2d between Fe^+ and butane (c), and reaction 10 between $FeCO^+$ and 1,3-butadiene (d).

spectra for the products of reactions 6 and 7 are superimposable and are therefore represented as a single spectrum in Figure 3b.

Figure 2 compares the CID spectra of $FeC_4H_8^+$ formed by the reaction of Fe^+ and 2-methylpropane, reaction 1b, to that of the product of the reaction 4 between $FeCO^+$ and 2-methylpropene. The agreement between the spectra in Figure 2 is not exact, but the difference from the CID spectra of the remaining $FeC_4H_8^+$ ions is dramatic. The two ions may differ somewhat in energy content, but they are essentially the same structure. Besides Fe^+, the more significant ions in the CID spectra represent the loss of methane and of C_3H_5 radical from the complex. This is consistent with the (2-methylpropene)iron(+) structure VII for the product of both (1b) and (4). Structure VII is expected for the product of (1b) if it proceeds by the mechanism outlined in Scheme II. It is also the structure expected for the product of reaction 4 if its proceeds as a simple ligand substitution. The dominance of the Fe^+ fragment in the CID spectra indicates that 2-methylpropene largely retains its integrity in the complex. The minor processes of CH_4 and C_3H_5 loss can be interpreted in terms of attack of Fe^+ on the C–C single bond in 2-methylpropene.

The (2-methylpropene)iron(+) formed in (4) shows slightly more of the Fe^+ fragment and slightly less of the high-energy $FeC_4H_7^+$ and $FeCH_3^+$ fragments on CID than does the Fe-$((CH_3)_2CCH_2)^+$ formed in reaction 1b. This can be explained in terms of the energy content of the ions. If reactions 1b and 4 produce the same $FeC_4H_8^+$ ion, then reaction 1b is 1.48 eV more exothermic than (4) for the ground-state reactants.[18,19] It might therefore be expected that reaction 1b forms the more energetic
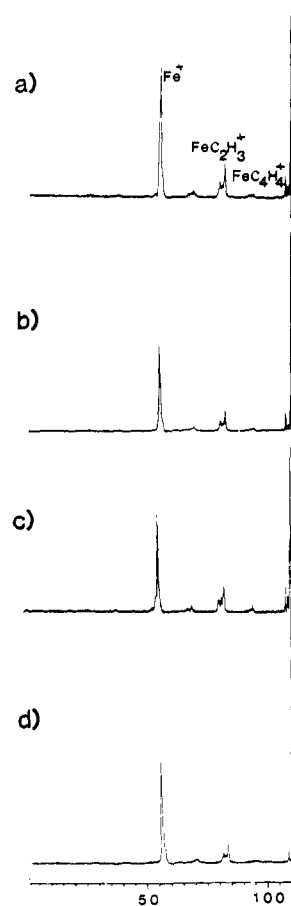
product, which gives more of the high-energy fragments on CID.

The CID spectra of $FeC_4H_8^+$ complexes formed by reactions 2c and 5–8 are shown in Figure 3. Reaction 5 occurs in two successive bimolecular steps. $FeC_4H_8^+$ is one of several products of reaction between Fe^+ and cyclopentanone. The spectra can be interpreted in terms of structures XII, XVII, and XIX.

The bis(ethylene) complex, XII, is certainly the structure expected for the product of reaction 5 between $Fe(CO)_2^+$ and C_2H_4. The CID spectrum of the product of reaction 5 shown in Figure 3a is dominated by C_2H_4 loss, which supports structure XII.

Several observations suggest an iron butadiene dihydride, XVII, as the common structure of the products of reactions 6 and 7 between $FeCO^+$ and the 1- and 2-butenes. The two ions give identical CID spectra (Figure 3b) dominated by H_2 loss. Structure XVII should lose H_2 readily and can be formed from both sets of precursors via the allylic intermediate XVI. In addition, the remainder of the CID spectrum besides H_2 loss is very similar to the CID spectrum of the species to which we assign the (butadiene)iron(+) structure below (see Figure 4 and Table III).

The major features of the CID spectrum of the product of reaction 8 between Fe^+ and cyclopentanone (Figure 3c) are loss of H_2 and loss of C_2H_4. This implies that some product ions have the bis(ethylene) structure (XII) and others have the iron butadiene dihydride structure (XVII). However, no linear combination of spectra 3a and 3b gives a good match to spectrum 3c. A straightforward explanation for this is that the ions formed in reaction 8 include at least some ions of a structure different from XII and XVII. The best candidate for such a structure is the

(19) Based on thermochemical data on organic ions: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6*, Suppl. 1.

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Table III. CID Spectra of FeC$_4$H$_6$⁺ Isomers from Ion-Molecule Reactions[a]

fragments	reactants			
	Fe⁺ + n-C$_4$H$_{10}$	Fe⁺ + 1-C$_4$H$_8$	Fe⁺ + 2-C$_4$H$_8$	Fe(CO)⁺ + 1,3-C$_4$H$_6$
FeC$_4$H$_5$⁺	0.07	0.05	0.04	0.02
FeC$_4$H$_4$⁺	0.11	0.08	0.10	0.07
FeC$_3$H$_2$⁺	0.03	0.02	0.02	0.01
FeC$_2$H$_3$⁺	0.11	0.12	0.12	0.10
FeC$_2$H$_2$⁺	0.06	0.05	0.05	0.04
FeC$_2$H⁺	0.05	0.06	0.06	0.05
FeCH⁺	0.03	0.03	0.03	0.02
FeH⁺	0.10	0.11	0.09	0.11
Fe⁺	0.43	0.49	0.50	0.56

[a] Relative intensities normalized by setting the total of the fragment ion intensities equal to 1.

Table IV. CID Spectra of Fe(C$_3$H$_6$)⁺ Isomers from Ion-Molecule Reactions[a]

fragments	reactants		
	Fe⁺ + (CH$_3$)$_3$CH	Fe⁺ + n-C$_4$H$_{10}$	Fe(CO)⁺ + C$_3$H$_6$
FeC$_3$H$_5$⁺	0.03	0.03	
FeC$_3$H$_3$⁺	0.11	0.11	0.11[b]
FeC$_2$H$_3$⁺	0.02	0.02	
FeC$_2$H⁺	0.02	0.02	
FeCH$_3$⁺	0.04	0.04	0.06[b]
FeCH$_2$⁺	0.03	0.03	
FeH⁺	0.08	0.09	0.10[b]
Fe⁺	0.66	0.67	0.74[b]

[a] Relative intensities normalized by setting the total of the fragment ion intensities equal to 1. [b] The error in these relative intensities is ±0.036 as a result of the low intensity of the primary ion.

metallocycle XIX. Insertion of the metal into the bonds adjacent to the carbonyl to give XIX is the simplest mechanism for reaction 8.
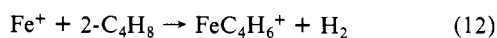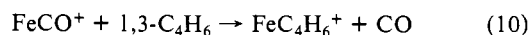
Reaction 8 is 1.72 eV more exothermic than reaction 7 and 1.61 eV more exothermic than reaction 5 relative to a common ionic product and ground-state reactants.[18,19] The FeC$_4$H$_8$⁺ produced in (8) may, therefore, have significantly more internal energy than the FeC$_4$H$_8$⁺ ions produced in (5) and (7). As indicated above, the CID spectrum of the product of reaction 8 fails to match any linear combination of the CID spectra of the products of reactions 5 and 7. This could be the result of the greater internal energy in the product of reaction 8 rather than the presence of a metallacyclic structure, XIX, among the ions formed in reaction 8. Note, however, that the ratio of the intensities of the FeC$_2$H$_4$⁺ fragment to that of the FeC$_2$H$_3$⁺ fragment in the CID of the product of reaction 8, 6.1, is greater than or equal to that ratio of the CID of the products of (5), 6.1, or (7), 0.25. This is the reverse of the expected effect. Increased internal energy should enhance the high-energy FeC$_2$H$_3$⁺ ion and diminish the low-energy FeC$_2$H$_4$⁺ ion. Some mixture of structures including metallacyclic structure XIX for the product of reaction 8, therefore, is the better explanation of its CID.

Ions of both structure XII and structure XVII are formed in reaction 2c between Fe⁺ and butane. The CID spectrum of that species shows both the C$_2$H$_4$ loss characteristic of XII and the H$_2$ loss characteristic of XVII. Furthermore, a combination of 33% of spectrum 3a and 67% of spectrum 3b gives a very good match for spectrum 3d, as is evident in Table II. This implies that Fe⁺ reacts with butane to form FeC$_4$H$_8$⁺, 33% of which has the bis(ethylene) structure XII and 67% of which has the iron butadiene dihydride structure XVII. The same result is obtained from CID spectra taken at two different butane pressures, which eliminates the possibility that the result is effected by reaction 9.

$$\text{FeC}_2\text{H}_4{}^+ + n\text{-C}_4\text{H}_{10} \rightarrow \text{Fe}(\text{C}_2\text{H}_4)_2{}^+ + \text{C}_2\text{H}_6 \qquad (9)$$
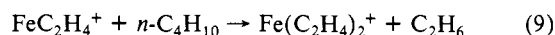
A mechanism by which a bis(ethylene) complex might be formed in the reactions of butane with Fe⁺ is shown in Scheme III. This mechanism has been suggested for the reaction of Ni⁺ with butane to form a bis(ethylene) complex of Ni⁺.[11] In the case of Ni⁺ no other NiC$_4$H$_8$⁺ structure seems to be formed in reaction with butane. This implies that the reactivity of a C–C bond toward Ni⁺ is greater than that of a C–H bond. In the case of Fe⁺, the formation of both the bis(ethylene) and the iron butadiene dihydride structures indicates that the reactivity of a C–H bond toward Fe⁺ is comparable to that of a C–C bond.

Fe(C$_4$H$_6$)⁺. The FeC$_4$H$_6$⁺ ion formed in reaction 2d shares a common structure with the FeC$_4$H$_6$⁺ ions formed in reactions 10–12. The CID spectra of the FeC$_4$H$_6$⁺ ions are shown in Figure

$$\text{FeCO}^+ + 1,3\text{-C}_4\text{H}_6 \rightarrow \text{FeC}_4\text{H}_6{}^+ + \text{CO} \qquad (10)$$

$$\text{Fe}^+ + 1\text{-C}_4\text{H}_8 \rightarrow \text{FeC}_4\text{H}_6{}^+ + \text{H}_2 \qquad (11)$$

$$\text{Fe}^+ + 2\text{-C}_4\text{H}_8 \rightarrow \text{FeC}_4\text{H}_6{}^+ + \text{H}_2 \qquad (12)$$

4 and tabulated in Table III. The dominant feature of all these

spectra is loss of C$_4$H$_6$. Of the remaining smaller features the most important is FeC$_2$H$_3$⁺. No reaction is observed between Fe⁺ and 1,3-butadiene. These results show that all the FeC$_4$H$_6$⁺ species are a complex of Fe⁺ with butadiene. The mechanisms by which such a complex is formed from reactions 11 and 12 involve the allylic intermediate XVI and the dihydride XVII in Scheme IV.

It is evident from Table III that the CID spectra of the various FeC$_4$H$_6$⁺ vary slightly from one another. The CID spectra of the two FeC$_4$H$_6$⁺ species formed in reactions 11 and 12 between Fe⁺ and the butenes are essentially the same. The CID spectrum of the product of reaction 10 between FeCO⁺ and 1,3-butadiene shows larger Fe⁺ and smaller FeC$_4$H$_5$⁺ peaks than the spectra of the products of reactions 11 and 12. This is the result of the fact that reaction 10 is 1.52–1.59 eV less exothermic (for ground-state species) than reactions 11 and 12. The CID of the FeC$_4$H$_6$⁺ product of reaction 2d between Fe⁺ and butane has a smaller Fe⁺ peak and a larger FeC$_4$H$_5$⁺ and FeC$_4$H$_4$⁺ peaks than the spectrum of the product of reaction 10. This is not the result of the relative exothermicity of reaction 2d but probably a feature of the mechanism of the reaction. Reactions 2d and 10 have approximately the same exothermicity for ground-state species. Reaction 2d involves breaking four covalent bonds and making two new ones as well as substantial geometric changes. These changes might well leave the various internal modes of the product in excited states.

FeC$_3$H$_6$⁺ and FeC$_2$H$_4$⁺. The remaining ions formed in the reaction of Fe⁺ with the butanes are the FeC$_3$H$_6$⁺ products formed in reactions 1a and 2b and the FeC$_2$H$_4$⁺ ion formed in reaction 2a. The CID spectra of the FeC$_3$H$_6$⁺ ions formed in (1a) and (2b) is compared with that of the ion formed in reaction 13 in
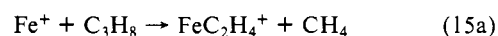
$$\text{FeCO}^+ + \text{C}_3\text{H}_6 \rightarrow \text{FeC}_3\text{H}_6{}^+ + \text{CO} \qquad (13)$$

Table IV. These ions all seem to have the same structure. The CID spectra are dominated by loss of C$_3$H$_6$. Of the minor decomposition channels, loss of H$_2$ and loss of H + H$_2$ are the more important. Propene does not react with Fe⁺ to an observable extent. These observations indicate that all the FeC$_3$H$_6$⁺ species are predominantly complexes of intact propene with Fe⁺. Some insertion of Fe⁺ into the allylic C–H bond may occur so that a structure consisting of Fe⁺ with hydride and allyl ligands may play a minor role.

The FeC$_2$H$_4$⁺ ion formed in reaction 2a and that formed in reaction 14 are indistinguishable by CID. The dominant fragment

$$\text{FeCO}^+ + \text{C}_2\text{H}_4 \rightarrow \text{FeC}_2\text{H}_4{}^+ + \text{CO} \qquad (14)$$
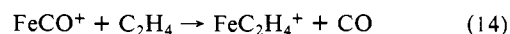
in the spectra is Fe⁺. Much smaller peaks appear for FeH⁺, FeCH$_2$⁺, and FeC$_2$H$_3$⁺. The FeC$_2$H$_4$⁺ ions are metal–ethylene complexes.

FeC$_3$H$_8$⁺, FeC$_2$H$_6$⁺, and FeCH$_4$⁺. Reaction 15 produces FeC$_2$H$_4$⁺ and FeC$_3$H$_6$⁺ in a ratio of about 7:3.[6] Neither C$_2$H$_6$

$$\text{Fe}^+ + \text{C}_3\text{H}_8 \rightarrow \text{FeC}_2\text{H}_4{}^+ + \text{CH}_4 \qquad (15a)$$

$$\rightarrow \text{FeC}_3\text{H}_6{}^+ + \text{H}_2 \qquad (15b)$$
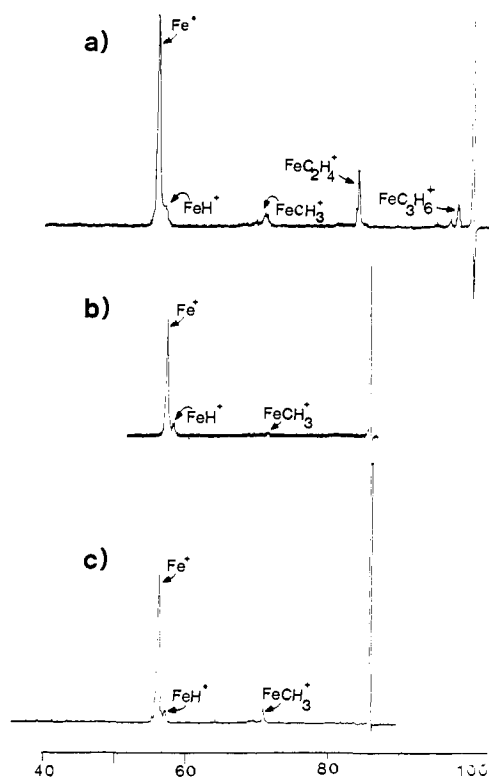
Figure 5. The collision-induced decomposition spectra of $Fe(C_3H_8)^+$ (m/z 100) and $Fe(C_2H_6)^+$ (m/z 86) formed in the ion source by ion-molecule reactions. The $Fe(C_3H_8)^+$ ion is formed by the reaction between $FeCO^+$ and propane (a). The two isomers of $Fe(C_2H_6)^+$ are formed by reaction of $FeCO^+$ with ethane (b) and reaction 16 of Fe^+ with acetone (c).

Table V. CID Spectra of $FeC_3H_8^+$ and $FeC_2H_6^+$ Ions Formed in Ion-Molecule Reactions[a]

| fragments	FeCO⁺ + C₃H₈ → FeC₃H₈ + CO	FeCO⁺ + C₂H₆ → FeC₂H₆⁺ + CO	Fe⁺ + (CH₃)₂CO → FeC₂H₆⁺ + CO
	reactions		
$FeC_3H_6^+$	0.07		
$FeC_3H_5^+$	0.03		
$FeC_2H_4^+$	0.16		
$FeCH_3^+$	0.04	0.03	0.08
$FeCH_2^+$	0.02		
FeH^+	0.06	0.09	0.07
Fe^+	0.62	0.88	0.85

[a] Relative intensities normalized by setting the total of the fragment ion intensities equal to 1.

nor CH_4 has been observed to react with Fe^+ at thermal energies. C_3H_8, C_2H_6, and CH_4 each react with $FeCO^+$, producing $FeC_3H_8^+$, $FeC_2H_6^+$, and $FeCH_4^+$, respectively. The CID spectra of $FeC_3H_8^+$ and $FeC_2H_6^+$ formed in this way are shown in parts a and b of Figure 5, respectively. Also shown in Figure 5 is the CID spectrum of the $FeC_2H_6^+$ ion formed in reaction 16.[20] The

$$Fe^+ + C_3H_6O \rightarrow FeC_2H_6^+ + CO \qquad (16)$$
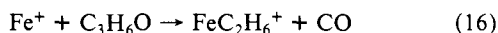
relative peak intensities for the spectra in Figure 5 are in Table V.

All three CID spectra are dominated by the Fe^+ fragment. The $FeC_3H_8^+$ spectrum has a sizable $FeC_2H_4^+$ peak and smaller peaks at FeH^+, $FeCH_3^+$, and $FeC_3H_6^+$. This suggests that species such as XX and XXI are formed to some extent in the reaction of

$$\text{H—Fe}^+\diagdown \qquad \text{CH}_3\text{—Fe}^+\text{—CH}_3$$
$$\text{XX} \qquad\qquad\quad \text{XXI}$$
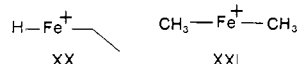
$FeCO^+$ with propane. These structures are expected to be intermediates along the two pathways leading to products in reaction

Table VI. CID Spectra of $FeC_3H_6O^+$ Isomers Formed From Ion-Molecule Reactions[a]

fragment	FeCO⁺ + (CH₃)₂CO	Fe(CO)₂⁺ + C₂H₆	Fe⁺ + CH₃COC₃H₇
	reactants		
$FeC_2H_6^+$	0.02		0.05
$FeCO^+$	0.21	0.85[b]	0.19
$FeCH_3^+$	0.13		0.17
$FeCH_2^+$	0.03		0.05
$FeCH^+$	0.01		0.03
Fe^+	0.52	0.15[b]	0.48
CH_3CO^+	0.02		0.03

[a] Relative intensities normalized by setting the total of the fragment ion intensities equal to 1. [b] The error in these relative intensities is ±0.05 as a result of low intensity of the primary ion.

15. As in the case of the butanes, the reaction between Fe^+ and propane seems to occur on the same potential surface as the CID of the $FeC_3H_8^+$ complex.

The CID spectrum of the $FeC_2H_6^+$ from reaction of ethane with $FeCO^+$ (Figure 5b) shows small FeH^+ and $FeCH_3^+$ fragment peaks in addition to the Fe^+ fragment peak. This CID spectrum is similar to that of the product of reaction 16 (Figure 5c) except that the latter has a significantly larger $FeCH_3^+$ peak. The difference between the two spectra could be a result of the difference in the internal energy of the two ions. Reaction 17 is 2.5

$$Fe^+ + C_3H_6O \rightarrow FeCO^+ + C_2H_6 \qquad (17)$$

eV exothermic for ground-state species.[20] That means that the $FeC_3H_6O^+$ complex formed from Fe^+ and acetone has as much as 2.5 eV more internal energy than that formed from $FeCO^+$ and C_2H_6. It is to be expected, then, that the product of reaction 16 has more internal energy than $FeC_2H_6^+$ formed in the reaction of $FeCO^+$ with C_2H_6. This would explain the difference in the CID spectra of the two $FeC_2H_6^+$ species if CH_3–Fe^+–CH_3 were a higher energy form of $FeC_2H_6^+$ than H–Fe^+–C_2H_5. The CID spectrum of the more energetic of the two $FeC_2H_6^+$ species would than be expected to show a larger $FeCH_3^+$ peak, which it does. Alternatively, CH_3–Fe^+–CH_3 certainly suggests itself as the most probable initial structure for the product of reaction 16. If an energy barrier separated CH_3–Fe^+–CH_3 from H–Fe^+–C_2H_5, then the CID results could be accounted for without supposing that CH_3–Fe^+–CH_3 is the higher energy structure. A CH_3–Fe^+–CH_3 species stable to rearrangement would be expected to produce $FeCH_3^+$ on collisional dissociation.

The CID spectrum of $FeCH_4^+$ formed in reaction between $FeCO^+$ and CH_4 shows only an Fe^+ fragment above the noise ($S:N \sim 20$). Evidently the C–H bonds in methane are unreactive toward Fe^+.
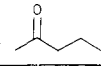
$FeC_3H_6O^+$. Ions of the $Fe(C_3H_6O)^+$ stoichiometry are formed in reactions 18–20. These ions are of interest since the addition

$$Fe(CO)_2^+ + C_2H_6 \rightarrow FeCOC_2H_6^+ + CO \qquad (18)$$

$$Fe(CO)^+ + C_3H_6O \rightarrow FeC_3H_6O^+ + CO \qquad (19)$$

$$Fe^+ + \text{2-pentanone} \rightarrow FeC_3H_6O^+ + C_2H_4 \qquad (20)$$

of CO to a complex of C_2H_6 with Fe^+ produces $FeC_3H_6O^+$. The effect of a CO on the interaction of Fe^+ and C_2H_6 may be reflected in the properties of the ions. The reactants of reaction 19 and that of reaction 20 are 0.62 and 2.35 eV, respectively, higher in energy than the reactants of (18) for ground-state species and a common product ion. The CID spectra of the products of (19) and (20) are very similar to one another and markedly different from the CID spectrum of the product of (18) (Figure 6 and Table VI). The structure for the latter is designated as $Fe(CO)(C_2H_6)^+$. The former indicates a mixture of structures such as CH_3–Fe^+–$COCH_3$ and a structure, $Fe(C_3H_6O)^+$, in which the acetone

(20) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360-7.

Table VII. CID Spectra of $FeC_5H_{10}O^+$ Isomers from Ion-Molecule Reactions[a]

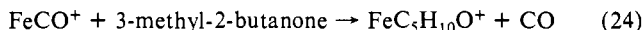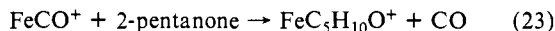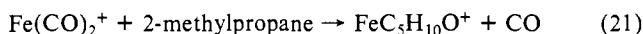|		reactants			
m/e	fragments[b]	$Fe(CO)_2^+$ + (2-methylpropane)	$Fe(CO)_2^+$ + (butane)	$FeCO^+$ + (2-pentanone)	$FeCO^+$ + (3-methyl-2-butanone)
140	$FeCOC_4H_8^+$			0.09	0.74
126	$FeCOC_3H_6^+$	0.06		0.65	0.03
114	$FeC_4H_{10}^+/FeC_3H_6O^+$	0.12	0.15	0.015	0.09
112	$FeC_4H_8^+/FeC_3H_4O^+$	0.07	0.02	0.002	0.008
111	$FeC_4H_7^+$	0.05	0.04		
110	$FeC_4H_6^+$		0.02	0.01	0.008
98	$FeC_3H_6^+/FeC_2H_4O^+$	0.08	0.04	0.02	
84	$FeCO^+/FeC_2H_4^+$	0.40	0.54	0.005	0.008
71	$FeCH_3^+$	0.04	0.02	0.04	0.03
57	FeH^+	0.02	0.04		
56	Fe^+	0.10	0.11	0.11	0.05

[a] Relative intensities normalized by setting the total of the fragment ion intensities equal to 1. [b] In case of ambiguous stoichiometry the more probable stoichiometry on mechanistic and energetic arguments is listed first.

molecule retains its integrity. The CID of this mixture of structures does show some sensitivity to the internal energy of the ion. On going from the CID of the product of reaction 19 to that of the product of the more exothermic reaction 20 the ratio of $FeC_2H_6^+$ to $FeCO^+$ fragment intensities increases from 0.11 to 0.26. Therefore, the fragmentation to form $FeC_2H_6^+$ is higher in energy than that to form $FeCO^+$.

It appears that the product of (18), $Fe(CO)(C_2H_6)^+$, does not readily rearrange to the (acetone)iron(+) or $CH_3-Fe^+-COCH_3$ structures formed in (19) and (20). This indicates a significant energy barrier to the formation of new C–C bonds involving the carbonyl carbon. That barrier is probably associated with the initial step of breaking the C–C bond in ethane.

The lowest energy pathway from $FeC_3H_6O^+$ to $FeCH_3^+$ forms CH_3CO as the neutral fragment. The low-energy pathway from $FeC_3H_6O^+$ to CH_3CO^+ forms $FeCH_3$ as a neutral product. Formation of $FeCH_3^+$ and CH_3CO^+ fragment ions in the CID of the products of reactions 19 and 20 involves competition between the $FeCH_3$ and $COCH_3$ for the charge. Observation of both ionic fragments indicates that $IP(FeCH_3) \approx IP(CH_3CO) = 6.78$ eV.[19] This implies that $D(Fe^+-CH_3) - D(Fe-CH_3) \approx 27.2$ kcal/mol. With the reported value of $D(Fe^+-CH_3) = 69 \pm 5$ kcal/mol,[5] this gives $D(Fe-CH_3) \approx 42$ kcal/mol.

$FeC_5H_{10}O^+$. Ions of this stoichiometry are formed in reactions 21–24. As is evident in Figure 7 and Table VII the CID spectra

$$Fe(CO)_2^+ + \text{2-methylpropane} \rightarrow FeC_5H_{10}O^+ + CO \qquad (21)$$

$$Fe(CO)_2^+ + \text{butane} \rightarrow FeC_5H_{10}O^+ + CO \qquad (22)$$

$$FeCO^+ + \text{2-pentanone} \rightarrow FeC_5H_{10}O^+ + CO \qquad (23)$$

$$FeCO^+ + \text{3-methyl-2-butanone} \rightarrow FeC_5H_{10}O^+ + CO \qquad (24)$$

of the products of the four reactions are quite distinct, suggesting different structures rather than just different internal energies. There is more than one stoichiometry possible for many of the fragments, but energetic and mechanistic considerations limit the possibilities considerably. In view of these considerations the conclusions discussed below suggest themselves.

The major peaks in the CID spectrum of the products of (21) and (22) correspond in mass to $FeCO^+$ (Figure 7c,d). Next in size are peaks corresponding in mass to $FeC_4H_{10}^+$ and Fe^+. This is what is similar to the CID spectrum of $Fe(CO)(C_2H_6)^+$ discussed above, and this indicates that a loosely bound $Fe(CO)(C_4H_{10})^+$ structure plays an important role in the ions formed in reactions 21 and 22. Smaller but significant peaks also appear to masses corresponding to FeH^+, $FeCH_3^+$, $FeC_3H_6^+$, $FeC_4H_8^+$, and in the case of the product of reaction 22, $FeC_4H_6^+$. These peaks represent a total of 0.224 and 0.140 of the fragment ion intensity in the spectra of the products of reactions 21 and 22, respectively. It is probable that the m/z 84 peak in the spectrum of the product of reaction 22 represents some $FeC_2H_4^+$ in addition to $FeCO^+$. These are the fragments observed in the CID of complexes of Fe^+ with 2-methylpropane and butane formed in
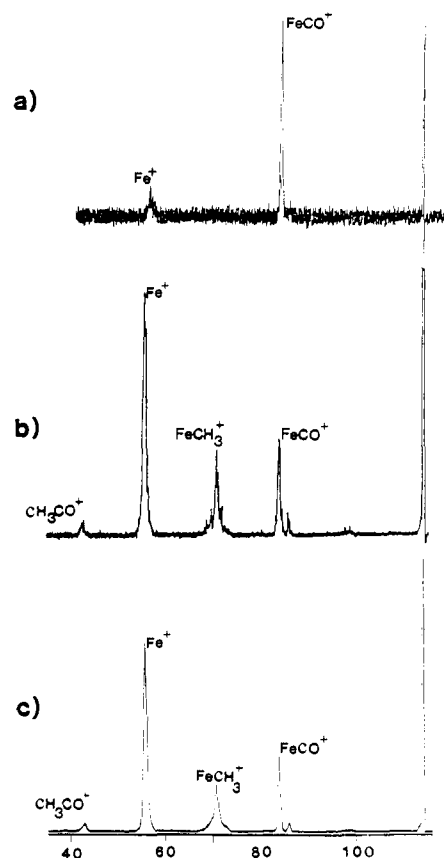

Figure 6. The collision-induced decomposition spectra of $Fe(C_3H_6O)^+$ (m/z 114) formed in the ion source by reaction 18 between $Fe(CO)_2^+$ and ethane (a), reaction 20 of Fe^+ with 2-pentanone (b), and reaction 19 of $FeCO^+$ with acetone (c).

the reactions of $FeCO^+$ with the butanes. This suggests that structures related to those postulated above for the $FeC_4H_{10}^+$ ions play some role in the $FeC_5H_{10}O^+$ ions formed in reactions 21 and 22. Species that we might designate $(H)Fe(t-C_4H_9)(CO)^+$ and $(CH_3)Fe(i-C_3H_7)(CO)^+$, for example, are probably present among the ions formed in reaction 21.

The CO ligand reduces but does not eliminate the susceptibility of Fe^+ to add to the C–C and C–H bonds in the butanes. The effect is not as pronounced as in the case of $Fe(CO)(C_2H_6)^+$, probably because the bonds in C_2H_6 are not as reactive as the bonds in the butanes. This effect of the CO ligand probably results from the change in the oxidation state of the metal that occurs with oxidative addition. Higher oxidation states of transition metals tend to form weaker bonds to CO so that oxidative addition of a C–H or C–C bond to the metal weakens the Fe^+–CO bond.[21]
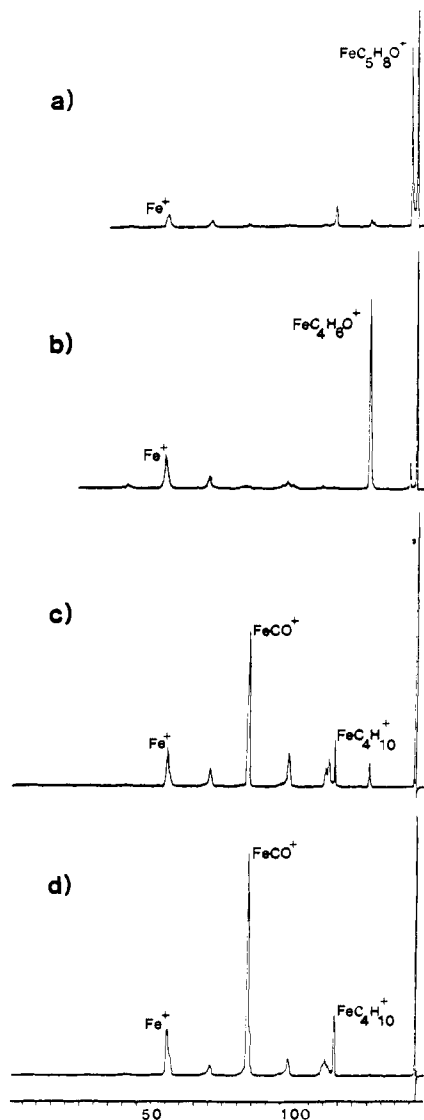
Figure 7. The collision-induced decomposition spectra of $Fe(C_5H_{10}O)^+$ (m/z 142) formed in the ion source by reaction 23 between $FeCO^+$ and 2-pentanone (a), reaction 24 of Fe^+ and 3-methyl-2-butanone (b), reaction 21 of $Fe(CO)_2^+$ with 2-methylpropane (c), and reaction 22 of $Fe(CO)_2^+$ with butane (d).

This gives rise to an energy barrier hindering such additions.

Several features of the spectra of the products of reactions 21 and 22 imply a second effect of the CO ligand. It appears that some structural arrangements occur that involve the CO in new bonds. A fragment corresponding in mass to $FeC_4H_7^+$ is a significant fragment in both spectra (0.04 and 0.05 of the total fragment intensity). No such fragment appears to a significant extent in the $FeC_4H_{10}^+$ CID spectra. Formation of $FeC_4H_7^+$ involves loss of three H atoms and a CO. The lowest energy combination of these neutrals is H_2 and HCO, indicating that a structure such as $C_4H_9-Fe^+-CHO$ occurs. Such a structure would result from insertion of $M-CO^+$ into a C–H bond. Another feature suggesting CO involvement is the significant $FeC_4H_6O^+$ peak (0.06 of the total fragment ion intensity) in the spectrum of the product of reaction 21. Such a peak is the strongly predominant feature of the CID of the product of reaction 23 between
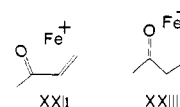
(21) When oxidized by halogens, for example, the bonds in $Fe(CO)_5$ are substantially weakened. The average Fe–CO bond strength in $Fe(CO)_5$ is 28.6 kcal/mol (see ref 19). The average Fe–CO bond strength in $Fe(CO)_4I_2$ is approximately 10 kcal/mol (Durant, P. J.; Durrant, B. "Introduction to Advanced Inorganic Chemistry"; Wiley: New York, 1962; p 111). Whether H^- behaves this way in neutral and anionic metal carbonyls in condensed phase is still under discussion. See: Pearson, R. G.; Walker, H. W.; Mauermann, H.; Ford, P. C. *Inorg. Chem.* **1981**, *20*, 2741-2743.

Table VIII. CID Spectra of $Fe_2(CO)_4C_4H_{10}^+$ Isomers Formed in Ion–Molecule Reactions[a]

		reactants	
m/e	fragments	$Fe_2(CO)_5^+$ + $(CH_3)_3CH$	$Fe_2(CO)_5^+$ + n-C_4H_{10}
280	$Fe_2(CO)_4C_4H_8^+$	0.031	0.053
254	$Fe_2(CO)_3C_4H_{10}^+$	0.039	0.056
252	$Fe_2(CO)_3C_4H_8^+$	0.034	0.036
250	$Fe_2(CO)_3C_4H_6^+$	0.014	

[a] Relative intensities normalized by setting the total of the fragment ion intensities equal to 1.

$FeCO^+$ and i-$C_3H_7COCH_3$ (see Table VII and Figure 7b). Insertion of $FeCO^+$ into the C–C bond in 2-methylpropane would give i-C_3H_7–Fe^+–$COCH_3$, which could readily rearrange to a complex of Fe^+ with i-$C_3H_7COCH_3$. Such a complex is presumably the initial product of reaction 24. The product of reaction 21 can then lose CH_4 on CID by the same mechanism that the product of reaction 24 loses CH_4 on CID. The CH_4 loss is absent in the CID spectrum of the product of reaction 22 between $Fe(CO)_2^+$ and butane (see Figure 7d and Table VII). This supports the $FeCO^+$ insertion as the origin of CH_4 loss in the product of reaction 23. $FeCO^+$ insertion into one of the bonds of butane cannot produce a complex of Fe^+ with i-$C_3H_7COCH_3$.

The CID spectrum of reaction 23 is dominated by an $FeC_4H_6O^+$ fragment corresponding to CH_4 loss. The CID spectrum of reaction 24 is dominated by an $FeC_5H_8O^+$ fragment, which corresponds to the lose of H_2. Ions of these stoichiometries are formed in the ion–molecule reaction of Fe^+ and the two $C_5H_{10}O$ isomers.[20] Structure XXII has been proposed for the $FeC_4H_6O^+$ species

XXII   XXIII

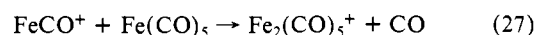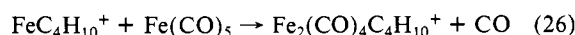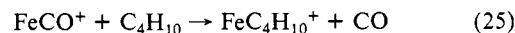observed in the spectrum for reaction 23.[20] The $FeC_5H_8O^+$ species observed in the CID spectrum of reaction 24 is thought to have structure XXIII.[20] These structures could result from a mechanism involving metal insertion followed by β-H atom shift. XXII is a probable structure of the $FeC_4H_6O^+$ formed by CID of the product of reaction 24, and XXIII is the probable structure of the $FeC_5H_8O^+$ formed by the CID of the product of reaction 23.
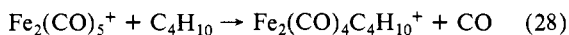
Breaking the ketone down into an alkane and a carbonyl ligand does not appear to be important in the complexes of Fe^+ with these ketones. The CID spectra of these complexes lack any $FeCO^+$ peak (Figure 7a,b). On the other hand incorporation of a carbonyl into the alkane does play a role in the $Fe(CO)(C_4H_{10})^+$ complexes formed by reaction of $Fe(CO)_2^+$ and the C_4H_{10} isomers. This suggests an energy barrier (perhaps a low barrier) between the (ketone)iron(+) structures. In addition, the (ketone)iron(+) structures are considerably lower in energy than the $Fe(CO)(C_4H_{10})^+$ structure, so that motion toward the latter structures is more probable than motion away from them.

It is worth comparing the product distributions of this study to the laser desorption experiments of the reactions between Fe^+ and the two $C_5H_{10}O$ isomers. The numbers in parentheses are for the reactions of Fe^+ formed by laser desorption from an iron surface. Fe^+ reacts with 3-methyl-2-butanone to give $FeC_4H_6O^+$ with relative abundances of 0.91 (0.87[20]) and 0.09 (0.13[20]), respectively. The major products of the reaction between Fe^+ and 2-pentanone are $FeC_3H_6O^+$ and $FeC_5H_8O^+$ in a ratio of 0.27:0.73 (0.21:0.79[20]). The good agreement between the two sets of numbers again suggests that the chemistry of Fe^+ formed by electron impact on $Fe(CO)_5$ is that of the ground-state ion.

$Fe_2(CO)_4C_4H_{10}^+$. Ions of this stoichiometry appear in mixtures of $Fe(CO)_5$ and butanes as a result of reactions 25–28. The CID

$$FeCO^+ + C_4H_{10} \rightarrow FeC_4H_{10}^+ + CO \qquad (25)$$

$$FeC_4H_{10}^+ + Fe(CO)_5 \rightarrow Fe_2(CO)_4C_4H_{10}^+ + CO \qquad (26)$$

$$FeCO^+ + Fe(CO)_5 \rightarrow Fe_2(CO)_5^+ + CO \qquad (27)$$

$$Fe_2(CO)_5{}^+ + C_4H_{10} \rightarrow Fe_2(CO)_4C_4H_{10}{}^+ + CO \quad (28)$$

of these ions is dominated by loss of C_4H_{10} and loss of C_4H_{10} plus one or more CO ligands. There are, however, other significant peaks as shown in Table VIII. These include peaks at masses corresponding to $Fe_2(CO)_4C_4H_8{}^+$, $Fe_2(CO)_3C_4H_{10}{}^+$, Fe_2-$(CO)_3C_4H_8{}^+$, and in the case of the ion formed from butane $Fe_2(CO)_3C_4H_6{}^+$. These ions correspond to loss of one H_2 molecule, one CO molecule, or both an H_2 and a CO molecule from the parent ion. Thus H_2 loss competes sucessfully with CO loss from both parent ions. This contrasts with the $FeCOC_4H_{10}{}^+$ ions in which CO loss always accompanied H_2 loss. The $Fe_2(CO)_4C_4H_{10}{}^+$ ions lose no CH_4 on CID. CO loss cannot be distinguished from C_2H_4 loss, but the CO loss peaks have very similar intensities in the CID spectra of both $Fe_2(CO)_4C_4H_{10}{}^+$ ions and no other cluster formed from 2-methylpropane loses C_2H_4. These observations indicate that the C–C bonds of the two C_4H_{10} isomers do not add to the metal centers in the $Fe_2(CO)_4C_4H_{10}{}^+$ clusters. The C–H bonds of the C_4H_{10} isomers, however, do appear to add to the metal centers in the clusters resulting in the elimination of H_2. This again is the in contrast to the $Fe(CO)C_4H_{10}{}^+$ complexes where addition of C–C bonds to the metal competes with addition of C–H bonds to the metal.

A primary difference between the mononuclear clusters and the binuclear clusters is the ability of the metal atoms to share charge density with one another. Thus the Fe atoms in Fe_2-$(CO)_4C_4H_{10}{}^+$ do not carry as much positive charge as the Fe atom in $Fe(CO)C_4H_{10}{}^+$. This accounts for the greater reactivity of the C–C bonds toward the metal in the mononuclear complex, since $D(Fe^+–CH_3) - D(Fe–CH_3) \approx 27.2$ kcal/mol (see above). The fact that the Fe atoms in the binuclear complex carry less charge then the Fe atom in the mononuclear complex probably affects the metal–carbonyl interaction. Addition of a C–H bond or formation of an H–Fe⁺–H moiety preliminary to H_2 loss oxidizes the Fe atom and probably weakens the bonds to CO ligands attached to the metal.[19] In a binuclear complex, the oxidation of the metal to which addition has occurred may be mediated by sharing electron density with the other metal atom or by transferring CO ligands to the less positively charge metal atom. The strength of the bonds to the CO ligands is thus preserved.

FeCH₂O⁺. An ion of the $FeCH_2O^+$ stoichiometry appeared in the mass spectrum of the $Fe(CO)_5$ mixture with acetone. The peak was considerably weaker than the other peak at the same nominal mass, $FeC_2H_6{}^+$, but at lower precise mass. The ion is presumably the product of reaction 29. An ion of the same

$$Fe^+ + C_3H_6O \rightarrow FeCH_2O^+ + C_2H_4 \quad (29)$$

$$FeCO^+ + CH_2O \rightarrow FeCH_2O^+ + CO \quad (30)$$
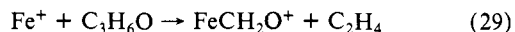
stoichiometry results from reaction 30. The CID spectra of the two ions are compared in Figure 8. Two distinct structures are certainly involved. The product of reaction 30 is an $Fe(CH_2O)^+$ complex bound by a charge–dipole interaction between an intact formaldehyde molecule and the Fe⁺ ion. That is indicated both by the CID which is dominated by an Fe⁺ fragment and by the nature of the reaction in which it is formed. The structure of the product of reaction 30 is XXIV. This is supported by the CID,

$$\begin{array}{c} H\,\diagdown \\ Fe^+{-}CO \\ H\,\diagup \end{array}$$
XXIV
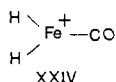
which has a large peak for $FeH_2{}^+$ and a slightly smaller Fe⁺ peak. Reaction 30 between Fe⁺ and C_3H_6O must involve the formation of the Fe–H bond. The absence of an $FeCO^+$ peak in the CID of the product of reaction 30 supports the conclusions reached in discussing the $FeCOC_4H_{10}{}^+$ and $Fe_2(CO)_4C_4H_{10}{}^+$ ions. That is, it involves the oxidative addition of H_2 (or C–H or C–C) to Fe⁺, which oxidizes the metal and reduces the bonding interaction with the CO ligand.

Summary and Conclusions

In isolated gas-phase complexes of Fe⁺ with a C_4H_{10} isomer, the alkane falls apart on the metal. The C–C and C–H bonds
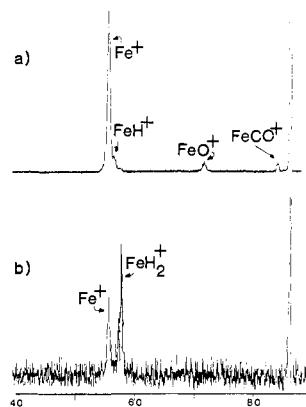

Figure 8. The collision-induced decomposition spectra of $Fe(H_2CO)^+$ (m/z 86) formed in the ion source by reaction 30 of $FeCO^+$ with formaldehyde (a) and reaction 29 of Fe⁺ with acetone (b).

add to the metal. This is the case in complexes with too little energy to dissociate as well as in complexes formed in bimolecular collisions of Fe⁺ and butane. As a result, the $FeC_4H_{10}{}^+$ species formed from 2-methylpropane and butane have distinct structures quite different from one another.

The reaction of Fe⁺ with 2-methylpropane produces $FeC_4H_8{}^+$ and $FeC_3H_6{}^+$. The $FeC_4H_8{}^+$ is a complex of Fe⁺ with 2-methylpropene. The $FeC_3H_6{}^+$ is a complex of Fe⁺ with propene. The reaction of Fe⁺ with butane produces $FeC_4H_8{}^+$, $FeC_4H_6{}^+$, $FeC_3H_6{}^+$, and $FeC_2H_4{}^+$. The $FeC_4H_8{}^+$ is a 2:1 mixture of two structures. The predominant structure might be characterized as a dihydride of Fe⁺ with a butadiene ligand. The other structure is a bis(ethylene) complex of Fe⁺. The $FeC_4H_6{}^+$ is an Fe⁺–(butadiene) complex. The $FeC_3H_6{}^+$ is an Fe⁺–(propene) complex. The $FeC_2H_4{}^+$ is an Fe⁺–(ethylene) complex. The structure of the products of reaction between Fe⁺ and the butanes is consistent with the mechanisms outlined in Schemes I–IV.

The interaction between Fe⁺ and the smaller alkanes is not as strong. C_3H_8 appears to fall apart to some extent in the $FeC_3H_8{}^+$ complex. Both the C–C bond and a C–H bond add to the metal. The addition products, however, may not be much lower in energy than a loosely bound complex of Fe⁺ with the intact propane. This is supported by the fact that the CID of the $FeC_3H_8{}^+$ complex is dominated by the Fe⁺ fragment. The products of reaction between Fe⁺ and C_3H_8 are an Fe⁺–(propene) complex and an Fe⁺–(ethylene) complex.

Some addition of both the C–H and C–C bonds in ethane occurs in the $FeC_2H_6{}^+$ complex. A loosely bound complex of intact C_2H_6 with Fe⁺ appears to be lower in energy than either addition product. The lowest energy form of the $FeCH_4{}^+$ complex is a loosely bound complex of CH_4 and Fe⁺. The C–H bond in methane does not seem to be reactive toward Fe⁺.

The reactivity of C–C and C–H bonds in the alkanes toward the Fe⁺ is related to their bond strengths. An order of reactivity can be assigned on the basis of the extent to which cleavage a particular bond competes with other processes in the various CID spectra. For C–C bonds the order of decreasing reactivity is CH_3-2-$C_3H_7 \approx C_2H_5$-$C_2H_5 \approx CH_3$-1-$C_3H_7 > CH_3$-$C_2H_5 > CH_3$-CH_3. For C–H bonds the order of decreasing reactivity is H-t-$C_4H_9 >$ H-sec-$C_4H_9 >$ H-2-$C_3H_7 >$ H-$C_2H_5 >$ H-CH_3. In each case reactivity decreases as bond strength increases. This is the trend expected for the oxidative addition mechanisms postulated. The reactivity of the C–C bonds in propane slightly exceeds that of the C–H bonds. That also seems to be true of butane. The H-t-C_4H_9 and CH_3-i-C_3H_7 bonds seem to be of comparable reactivity. The H–C_2H_5 bond is more reactive than the CH_3–CH_3 bond.

The butenes react with Fe⁺ to form $FeC_4H_6{}^+$. The structure of these $FeC_4H_6{}^+$ species is that of a complex of 1,3-butadiene with Fe⁺.

The ions produced by displacement of CO from $Fe(CO)_2{}^+$ by an alkane assume several kinds of structures. Alkanes retain their

integrity in complexes with $FeCO^+$ to a greater extent than they do in complexes with Fe^+. Oxidative addition of bonds in the alkane reduces the bonding between Fe^+ and CO. The presence of the CO ligand may therefore inhibit such oxidative additions. $Fe(CO)(C_2H_6)^+$ is the only structure observed for the ion formed by displacement of CO from $Fe(CO)_2^+$ by ethane.

$Fe(CO)(C_4H_{10})^+$ is the major structure observed for the ion formed by displacement of a CO from $Fe(CO)_2^+$ by either butane. In the case of these complexes there is some addition of butane bonds to the metal. Addition of C–H bonds is more important than addition of C–C bonds. This may also reflect the nature of the interaction between Fe^+ and CO, since addition of C–C and C–H bonds is competitive in complexes of Fe^+ with the butanes. Addition of C–H bonds to the metal in the complexes of $FeCO^+$ with butanes lead to H_2 loss upon collisional activation. The loss of only H_2 is not observed, however. CO loss always accompanies H_2 loss. This substantiates the assertion that addition of C–H bond to Fe^+ weakens the bond between Fe^+ and a CO ligand. There is also evidence for $FeCO^+$ insertion into the bonds of the butanes. $FeCO^+$ inserts into C–H bonds in both butanes and into the C–C bond in 2-methylpropane.

Isomers of the (carbon monoxide)(alkane)iron(+) complexes result from displacement of CO from $FeCO^+$ by an appropriate ketone. The structure of these (ketone)iron(+) complexes is strongly influenced by the strength of the interaction between Fe^+ and unsaturated ketones. The 3-methyl-2-butanone complex, for example, seems to assume a $(CH_3)(H)(Fe^+)$(1-butene-3-one) structure. Such structures are stable with respect to rearrangement to isomeric $(CO)(Fe^+)$(alkane) structures. In the complex of Fe^+ with acetone there is rearrangement to $CH_3–Fe–COCH_3^+$ or $Fe(CO)(C_2H_6)^+$, but much of the time the acetone remains intact. $Fe_2(CO)_4(C_4H_{10})^+$ has that structure predominantly. Some of a structure that might be designated $Fe_2(CO)_4(C_4H_8)(H)(H)^+$ is formed. This structure is characterized by H_2 loss on collisional activation. The loss of CO and two H_2 molecules distinguishes the $Fe_2(CO)_4(C_4H_{10})^+$ complex made from butane from that made from 2-methylpropane. Some of the collisionally activated binuclear clusters lose only an H_2 molecule and no CO ligands. This implies that the metal–carbonyl interaction is not weakened much by the addition of a C–H bond to one of the metals in these binuclear complexes. This contrasts with the case of the $FeCO^+$ complexes with the butanes.

Two structures are observed for $FeCH_2O^+$. One might be designated as $Fe(CH_2O)^+$ and the other as $Fe(H)(H)(CO)^+$. Only CO loss and CO loss accompanied by H_2 loss folllow collisional activation of $Fe(H)(H)(CO)^+$. This confirms that oxidative addition to Fe^+ weakens the interaction between the Fe^+ and an attached CO ligand. The two structures are formed in different reactions and do not seem to interconvert once formed. A substantial energy barrier exists between them. Finally, it is possible from the CID spectra of the complexes of Fe^+ with butanes and acetone to ascertain that $IP(FeCH_3) = IP(CH_3CO) = 6.78$ eV.[19] This implies that $D(Fe^+–CH_3) – D(Fe–CH_3) = 27.2$ kcal/mol. Combined with $D(Fe^+–CH_3) = 69 \pm 5$ kcal/mol, this gives $D(Fe–CH_3) \approx 42$ kcal/mol.

There are few data on the condensed-phase chemistry of ligand-free transition-metal atoms with alkanes to which the present results might be compared. In addition to the reactions of Ni clusters and Zr atoms, photoexcited transition-metal atoms have been reported to react with methane by metal insertion into the

C–H bond.[22,23] This oxidative addition and the reverse reductive elimination appear to have an activation energy. At least both processes require photoactivation.[23] The present results indicate that the atomic metal ion Fe^+ appears to encounter only small or nonexistent barriers in inserting into C–H and C–C bonds in the C_4H_{10} isomers. These insertion reactions appear to be facile even in the relatively low-energy $FeC_4H_{10}^+$ complexes formed by reaction of $FeCO^+$ with the C_4H_{10} isomers.

The effect of adding a CO ligand to a metal–alkane complex has not been investigated much in the condensed phase, although $Fe(CO)_4CH_4$ has been reported.[24] In this case the bonding mode is thought to be Fe–H–C.[24] Reductive elimination of alkane from the metal complexes containing two CH_3 ligands, two H ligands, or one CH_3 ligand and one H ligand has recently received theoretical examination.[25] Both theory and experiment tend to suggest that electronegative ligands raise the activation energy. Only if CO is considered an electronegative ligand is this consistent with the present results, which suggest that ease of oxidative addition of C–C and C–H bonds in alkanes to Fe^+ is diminished by a CO ligand. Oxidative addition is the microscopic reverse of reductive elimination, and a high-energy transition state for one implies a high-energy transition state for the other.

The mechanism by which C–H bonds in alkanes are attacked by coordinatively unsaturated metal atoms at surfaces has received considerable study.[26] It is generally observed that alkane C–H bonds and not alkane C–C bonds add to a coordinatively unsaturated metal atoms at surfaces. In the gas phase we observe that C–H bonds add to the metal atoms in ionic clusters containing two Fe atoms, but C–C bonds add preferentially to the metal in gaseous ionic clusters containing one Fe atom. Therefore, the present gas-phase results imply that a metal–metal bond changes the interaction of an Fe atom with an alkane, enhancing the reactivity of the C–H bonds relative to the reactivity of the C–C bonds. Since even on a nonmetallic support a metal atom at a surface is usually bound to another metal atom, a similar effect could account for the relative reactivity of alkane C–C and C–H bonds toward metals at a surface.

Note Added in Proof. CID of $FeC_4D_{10}^+$ prepared from $(CD_3)_3CD$ shows that the m/z 57 fragment in the CID of the unlabeled analogue is FeH^+ and not $C_4H_9^+$. If this fragment originates from structure V, arguments analogous to those applied to $CH_3–Fe^+–i-C_3H_7$ give $IP(FeH) < IP(t-C_4H_9) = 6.70$ eV (ref 17) and from $D(Fe^+–H) = 58 \pm 5$ kcal/mol (ref 5) $D(Fe–H) < 29$ kcal/mol.

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