Heteronuclear Diatomic Transition-Metal Cluster Ions in the Gas Phase. Reactions of $CuFe^+$ with Hydrocarbons

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Abstract: The reactions of $CuFe^+$ with a variety of hydrocarbons and oxygenated species were studied with Fourier transform mass spectrometry. $CuFe^+$ is unreactive with linear (C_1–C_6) and cyclic (C_3–C_6) alkanes. However, it does react with aliphatic alkenes which contain a linear C_4 unit, chiefly by dehydrogenation. The only aliphatic alkene in which C–C bond cleavage is observed is 2,3,3-trimethyl-1-butene, yielding methane elimination. The secondary reactions of the aliphatic alkenes generally yield more dehydrogenation than the primary reactions. Ion–molecule reactions, collision-induced dissociation, and photodissociation studies yield $D°(Cu^+-Fe) = 53 \pm 7$ kcal/mol and $D°(Fe^+-Cu) = 56 \pm 7$ kcal/mol. Finally, reaction between $CuFe^+$ and ethylene oxide yields both $CuFeCH_2^+$ and $CuFeO^+$, indicating $D°(CuFe^+-CH_2) > 79$ kcal/mol and $D°(CuFe^+-O) > 85$ kcal/mol, respectively.

Small, bare transition-metal clusters have recently become the focus of intense investigations[1] due to their importance in such areas as astronomy, homogeneous nucleation,[2] and heterogeneous catalysis.[3] These studies have been directed primarily toward obtaining information on both the physical and chemical properties of the clusters in an attempt to better understand the processes which occur on metal surfaces.

Gas-phase ion techniques have been shown to be ideally suited for the study of bare, transition-metal cluster ions. Several of the metal cluster ions reported have been generated by multiphoton ionization[4] or electron impact[5] of multinuclear metal carbonyl complexes. The latter method has been utilized with ion cyclotron resonance spectroscopy and ion-beam techniques, for example, to generate and study Co_2^+ [6] and Mn_2^+.[6-8] Smalley and others have recently developed supersonic beam expansion techniques which show tremendous potential for the generation and study of metal clusters over a wide range of sizes.[9] Another promising

technique for studying metal cluster ions involves the use of a SIMS source to sputter metal ions from a metal substrate. Freas and Campana, for example, have used this technique to study the ion–molecule reactions of copper cluster ions ($[Cu_n]^+$: $n = 1$–11).[10]

Recently, we reported a technique for in situ synthesis of bare homonuclear and heteronuclear metal cluster ions in the gas phase using Fourier transform mass spectrometry–collision-induced dissociation (FTMS–CID).[11] This technique has allowed examination of the photodissociation and reactivity of $CoFe^+$ [12] and VFe^+.[13] In this paper, we extend our survey of diatomic cluster ions to include the reactivity of $CuFe^+$ with alkanes, alkenes, and a few oxygenated compounds.

Experimental Section

The theory and instrumentation of Fourier transform mass spectrometry (FTMS) have been discussed elsewhere.[14] All experiments were performed with a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail[15] and equipped with a 5.2 cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.85 T. The cell was constructed in our laboratory and utilizes two 80% transmittance stainless steel screens as the transmitter plates. A copper rod with a small hole ($\sim$1 mm in diameter) bored through the center was supported on the transmitter plate nearest the laser. Cu^+ was generated by focussing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 532 nm) near the bored hole of the copper rod. Details of the laser ionization technique have been described elsewhere.[16]

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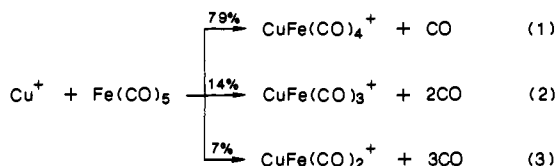
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Chemicals were obtained commercially in high purity and were used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensible gases. Fe(CO)$_5$ was introduced into the vacuum chamber via a pulsed valve as described previously.[17] The hydrocarbon reagents were added at a static pressure of $\sim 3 \times 10^{-7}$ Torr. Argon was used as the collision gas for collision-induced dissociation (CID) at a total pressure of $\sim 4 \times 10^{-6}$ Torr. A Bayard-Alpert ionization gauge was used to monitor the pressure.
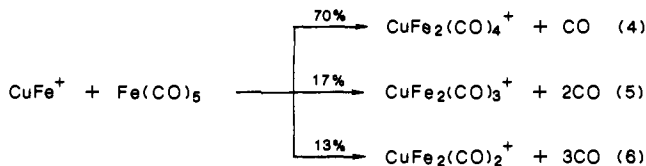
Details of the CID experiments have previously been discussed.[18] The collision energy of the ions can be varied (typically between 0 and 100 eV) from which plots of CID product ion intensities vs. ion kinetic energy can be made. The spread in ion kinetic energy is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.[19]

CuFe$^+$ was generated and studied by the following procedure in analogy to earlier studies of CoFe$^{+\,12}$ and VFe^{+}.[13] Laser desorbed copper ions of both isotopes 63 and 65 were formed. Before reactions could occur, the ^{65}Cu$^+$ isotope was ejected with a double resonance pulse.[20] Next, the ^{63}Cu$^+$ isotope, hereafter referred to as Cu$^+$, was allowed to react with a pulse of Fe(CO)$_5$ displacing one or more carbonyls as shown in reactions 1–3.

$$
\text{Cu}^+ + \text{Fe(CO)}_5 \longrightarrow
\begin{cases}
\xrightarrow{79\%} \text{CuFe(CO)}_4{}^+ + \text{CO} & (1) \\
\xrightarrow{14\%} \text{CuFe(CO)}_3{}^+ + 2\text{CO} & (2) \\
\xrightarrow{7\%} \text{CuFe(CO)}_2{}^+ + 3\text{CO} & (3)
\end{cases}
$$

The product of reaction 1, CuFe(CO)$_4{}^+$, was accelerated to ~ 51 eV kinetic energy causing the carbonyls to be sequentially eliminated via inelastic collisions with the argon target gas. The resultant CuFe$^+$ ions were then isolated and allowed to react with other reagent gases. The relatively high static pressure of argon is believed to allow any excess energy of the cluster to be dissipated by thermal collisions. Under these conditions, CuFe$^+$ undergoes approximately 20 collisions with argon for every collision with hydrocarbon. Trapping times were varied typically between 3 ms and 3 s to yield linear kinetic plots over 2 half-lives of CuFe$^+$ suggesting predominantly ground-state species. However, the presence of a small population of excited ions cannot be completely ruled out. Figure 1 illustrates the multistep synthesis and reaction of CuFe$^+$ with cyclohexene.

The reaction of CuFe$^+$ with Fe(CO)$_5$ proceeds to eliminate one or more carbonyls, reactions 4–6. These reactions are competitive with the

$$
\text{CuFe}^+ + \text{Fe(CO)}_5 \longrightarrow
\begin{cases}
\xrightarrow{70\%} \text{CuFe}_2\text{(CO)}_4{}^+ + \text{CO} & (4) \\
\xrightarrow{17\%} \text{CuFe}_2\text{(CO)}_3{}^+ + 2\text{CO} & (5) \\
\xrightarrow{13\%} \text{CuFe}_2\text{(CO)}_2{}^+ + 3\text{CO} & (6)
\end{cases}
$$

hydrocarbon reactions and, therefore, the Fe(CO)$_5$ was pulsed in to avoid confusion. Interestingly, both CoFe$^{+\,12}$ and VFe$^{+\,13}$ react only very slowly with Fe(CO)$_5$ and did not interfere with the hydrocarbon reactions.

Results and Discussion

Reactions with Alkanes. CuFe$^+$ is unreactive with both linear (C$_1$–C$_6$) and cyclic (C$_3$–C$_6$) alkanes as has been seen with several other first-row metal dimers such as Co$_2{}^{+}$,[21] CoFe^{+},[12] and VFe^{+}.[13] Recently, however, RhFe$^+$, RhCo$^+$, and LaFe$^+$ have been found to react with these alkanes.[22] In addition, Fe$^+$ has been observed to react with alkanes via both C–H and C–C bond insertions.[23] Cu$^+$, however, has also been found to be unreactive with alkanes,

forming only adducts with no bond cleavage observed.[24]

Reactions with Alkenes. Table I summarizes the reactions of CuFe$^+$ with alkenes. The absence of an observed reaction implies a rate constant of $<10^{-12}$ cm^3 molecule^{-1} s^{-1}. One interesting trend observed in examining Table I is that, in general, more dehydrogenation occurs in the secondary reactions than in the primary reactions, implying that alkadiene ligands in some way activate the CuFe$^+$ cluster. Table II gives a summary of bond energy limits obtained from the observed reactions in this study.

Aliphatic C$_2$–C$_4$ Alkenes. No reaction is observed for ethene, propene, 2-methylpropene, and butadiene with CuFe$^+$. With the linear butenes, CuFe$^+$ is observed to eliminate H$_2$ exclusively, reaction 7. Observation of reaction 7 implies $D°$(CuFe$^+$–buta-

$$
\text{CuFe}^+ + n\text{-C}_4\text{H}_8 \longrightarrow \text{CuFeC}_4\text{H}_6{}^+ + \text{H}_2 \qquad (7)
$$
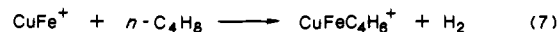
diene) > 29 kcal/mol.[25] In contrast, Fe$^+$ reacts with butene both by H$_2$ loss and C–C cleavage.[26]

Collisional activation of CuFeC$_4$H$_6{}^+$, formed in reaction 7, yields only elimination of C$_4$H$_6$ with CuFe$^+$ observed, implying $D°$(Fe$^+$–C$_4$H$_6$) $= 48 \pm 5$ kcal/mol[27] $< D°$(Fe$^+$–Cu) and $D°$-(Cu$^+$–C$_4$H$_6$) $< D°$(Cu$^+$–Fe). The absence of additional products is consistent with a butadiene species on the CuFe$^+$ cluster and with the fact that CuFe$^+$ is unreactive with butadiene.
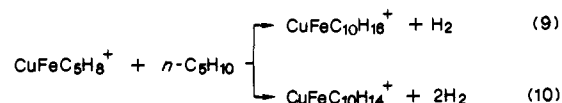
CuFeC$_4$H$_6{}^+$ undergoes a secondary reaction with linear butene, again by exclusive loss of one H$_2$ molecule, yielding a CuFeC$_8$H$_{12}{}^+$ species. CID of this product at low energies yields both dehydrogenation and (C$_2$H$_6$) elimination to give CuFeC$_8$H$_{10}{}^+$ and CuFeC$_6$H$_6{}^+$, respectively. At high kinetic energies, generation of CuFe$^+$ dominates. A Diels–Alder cycloaddition of bis(butadiene)CuFe$^+$ generating a 4-vinylcyclohexene complex can eliminate H$_2$ to generate CuFeC$_8$H$_{10}{}^+$. Further elimination of C$_2$H$_4$ would produce CuFe(benzene)$^+$. CID of bis(butadiene)Fe$^+$ has been shown to model the above Diels–Alder cycloaddition reaction, generating FeC$_6$H$_6{}^+$.[26]

Aliphatic C$_5$–C$_7$ Alkenes. CuFe$^+$ reacts with the linear pentenes yielding exclusively elimination of H$_2$, reaction 8, implying

$$
\text{CuFe}^+ + n\text{-C}_5\text{H}_{10} \longrightarrow \text{CuFeC}_5\text{H}_8{}^+ + \text{H}_2 \qquad (8)
$$

$D°$(CuFe$^+$–n-C$_5$H$_8$) > 26 kcal/mol.[25] This reaction is again different from Fe$^+$ reactions which involve mainly C–C cleavages.[26] CuFeC$_5$H$_8{}^+$, generated in reaction 8, undergoes facile elimination of H$_2$ upon collisional activation, presumably via dehydrocyclization to form a (cyclopentadiene)CuFe$^+$ complex. At high kinetic energies, elimination of C$_5$H$_8$ dominates with CuFe$^+$ observed. Evidence for the cyclopentadiene structure was obtained by isolation and collision-induced dissociation of the CID product, CuFeC$_5$H$_6{}^+$, which yields loss of CuH to form FeC$_5$H$_5{}^+$. This observation is identical with the collision-induced dissociation of CuFeC$_5$H$_6{}^+$ generated from the reaction of CuFe$^+$ with cyclopentene which is, presumably, (cyclopentadiene)CuFe$^+$.

The reaction of CuFeC$_5$H$_8{}^+$ with linear pentene yields elimination of H$_2$ and 2H$_2$, reactions 9 and 10. Collisional activation

$$
\text{CuFeC}_5\text{H}_8{}^+ + n\text{-C}_5\text{H}_{10} \longrightarrow
\begin{cases}
\text{CuFeC}_{10}\text{H}_{16}{}^+ + \text{H}_2 & (9) \\
\text{CuFeC}_{10}\text{H}_{14}{}^+ + 2\text{H}_2 & (10)
\end{cases}
$$

of CuFeC$_{10}$H$_{16}{}^+$ and CuFeC$_{10}$H$_{14}{}^+$ from reactions 9 and 10 yields sequential dehydrogenation to generate CuFeC$_{10}$H$_{12}{}^+$ with some CuFeC$_{10}$H$_{10}{}^+$ observed in low efficiency. The bis(cyclopentadiene)CuFe$^+$ structure, which is assumed for CuFeC$_{10}$H$_{12}{}^+$, dominates over the CuFeC$_{10}$H$_{10}{}^+$ at all energies.

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Table I. Distribution of Neutral(s) Lost for the Primary Reactions of $CuFe^+$ with Alkenes and the Secondary Reactions of $CuFeL^+$ Species[a]
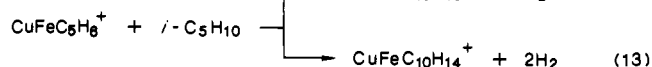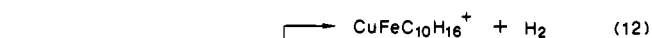
alkene	primary reactions			secondary reactions		
	neutral(s)	ion	rel %	neutral(s)	ion	rel %
ethene		no reaction				
propene		no reaction				
2-methylpropene		no reaction				
1-butene	H_2	$CuFeC_4H_6^+$	100	H_2	$CuFeC_8H_{12}^+$	100
cis-2-butene	H_2	$CuFeC_4H_6^+$	100	H_2	$CuFeC_8H_{12}^+$	100
trans-2-butene	H_2	$CuFeC_4H_6^+$	100	H_2	$CuFeC_8H_{12}^+$	100
1,3-butadiene		no reaction				
1-pentene	H_2	$CuFeC_5H_8^+$	100	H_2	$CuFeC_{10}H_{16}^+$	15
				$2H_2$	$CuFeC_{10}H_{14}^+$	85
trans-2-pentene	H_2	$CuFeC_5H_8^+$	100	H_2	$CuFeC_{10}H_{16}^+$	55
				$2H_2$	$CuFeC_{10}H_{14}^+$	45
2-methyl-1-butene	H_2	$CuFeC_5H_8^+$	100	H_2	$CuFeC_{10}H_{16}^+$	43
				$2H_2$	$CuFeC_{10}H_{14}^+$	57
3-methyl-1-butene	H_2	$CuFeC_5H_8^+$	100	H_2	$CuFeC_{10}H_{16}^+$	39
				$2H_2$	$CuFeC_{10}H_{14}^+$	61
2-methyl-2-butene	H_2	$CuFeC_5H_8^+$	100	H_2	$CuFeC_{10}H_{16}^+$	53
				$2H_2$	$CuFeC_{10}H_{14}^+$	47
2-methyl-1,3-butadiene		no reaction				
1-hexene[b]	H_2	$CuFeC_6H_{10}^+$	34	$2H_2$	$CuFeC_{12}H_{18}^+$	77
	$2H_2$	$CuFeC_6H_8^+$	66	$2H_2$	$CuFeC_{12}H_{16}^+$	23
2,3-dimethyl-1-butene	H_2	$CuFeC_6H_{10}^+$	100	H_2	$CuFeC_{12}H_{20}^+$	10
				$2H_2$	$CuFeC_{12}H_{18}^+$	90
2,3-dimethyl-2-butene	H_2	$CuFeC_6H_{10}^+$	65	H_2	$CuFeC_{12}H_{20}^+$	21
				$2H_2$	$CuFeC_{12}H_{18}^+$	79
	Fe	$CuC_6H_{12}^+$	35			
2,3,3-trimethyl-1-butene	CH_4	$CuFeC_6H_{10}^+$	55	CH_4, H_2	$CuFeC_{12}H_{18}^+$	47
				CH_4, $2H_2$	$CuFeC_{12}H_{16}^+$	53
	Fe	$CuC_7H_{14}^+$	45			
cyclopentene	H_2	$CuFeC_5H_6^+$	100	H_2	$CuFeC_{10}H_{12}^+$	26
				$2H_2$	$CuFeC_{10}H_{10}^+$	35
				$(CuH_2 + H_2)$	$FeC_{10}H_{10}^+$	39
cyclohexene	$2H_2$	$CuFeC_6H_6^+$	85	$2H_2$	$CuFeC_{12}H_{12}^+$	100
	$(CuH_2 + H_2)$	$FeC_6H_6^+$	15			
1,3-cyclohexadiene	H_2	$CuFeC_6H_6^+$	26	Fe	$CuC_{12}H_{14}^+$	64
				(CuH_2)	$FeC_{12}H_{12}^+$	36
	Fe	$CuC_6H_8^+$	21			
	(FeH_2)	$CuC_6H_6^+$	33			
	(CuH_2)	$FeC_6H_6^+$	20			
1,4-cyclohexadiene	H_2	$CuFeC_6H_6^+$	13	Fe	$CuC_{12}H_{14}^+$	60
				(CuH_2)	$FeC_{12}H_{12}^+$	40
	Fe	$CuC_6H_8^+$	35			
	(FeH_2)	$CuC_6H_6^+$	34			
	(CuH_2)	$FeC_6H_6^+$	18			
benzene	Fe	$CuC_6H_6^+$	63			
	Cu	$FeC_6H_6^+$	28			
		$CuFeC_6H_6^+$	9			
toluene	Fe	$CuC_7H_8^+$	77			
	Cu	$FeC_7H_8^+$	23			
norbornadiene	C_2H_2	$CuFeC_5H_6^+$	55	Cu	$FeC_{12}H_{14}^+$	100
	Fe	$CuC_7H_8^+$	45			
cycloheptene	$2H_2$	$CuFeC_7H_8^+$	100		$CuFeC_{14}H_{20}^+$	34
				H_2	$CuFeC_{14}H_{18}^+$	66
cycloheptatriene	Fe	$CuC_7H_8^+$	20			
	Cu	$FeC_7H_8^+$	17			
	(CuH)	$FeC_7H_7^+$	63			

[a] Product distribution is reproducible to ±10%. [b] Secondary reaction ratio is calculated from the sum of both primary products.

The reactions with the three isopentenes all result in the exclusive loss of H_2, reaction 11, implying $D°(CuFe^+–i\text{-}C_5H_8) >$

$$CuFe^+ + i\text{-}C_5H_{10} \longrightarrow CuFeC_5H_8^+ + H_2 \qquad (11)$$
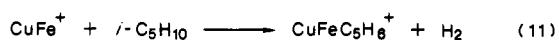
28 kcal/mol.[25] The secondary reactions of $CuFeC_5H_8^+$, generated from reaction 11, with the three isopentenes all result in the elimination of H_2 and $2H_2$, reactions 12 and 13. These results are also consistent with the reaction of $CoFe^+$ with 2-methyl-1-

$$CuFeC_5H_8^+ + i\text{-}C_5H_{10} \longrightarrow \begin{cases} CuFeC_{10}H_{16}^+ + H_2 & (12) \\ CuFeC_{10}H_{14}^+ + 2H_2 & (13) \end{cases}$$

butene, where an isoprene structure bound to $CoFe^+$ has been proposed.[12] CID of $CuFeC_5H_8^+$, generated in reaction 11, yields only facile elimination of C_5H_8 with $CuFe^+$ observed. Absence of dehydrogenation to form $CuFeC_5H_6^+$ indicates a different structure than seen with the linear pentene reactions. Also, the absence of reaction between $CuFe^+$ and 2-methyl-1,3-butadiene (isoprene) may also suggest a structure of isoprene bound to $CuFe^+$, structure I, for the product of reaction 11.

I
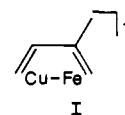
Collisional activation of $CuFeC_{10}H_{16}^+$ and $CuFeC_{10}H_{14}^+$ from reactions 12 and 13 results in sequential dehydrogenation to form predominantly $CuFeC_{10}H_{12}^+$ with some $CuFeC_{10}H_{10}^+$ also produced. From this result, structure differentiation between the reactions of $CuFe^+$ with linear pentenes vs. isopentenes is difficult, although it seems unlikely that rearrangements are occurring.
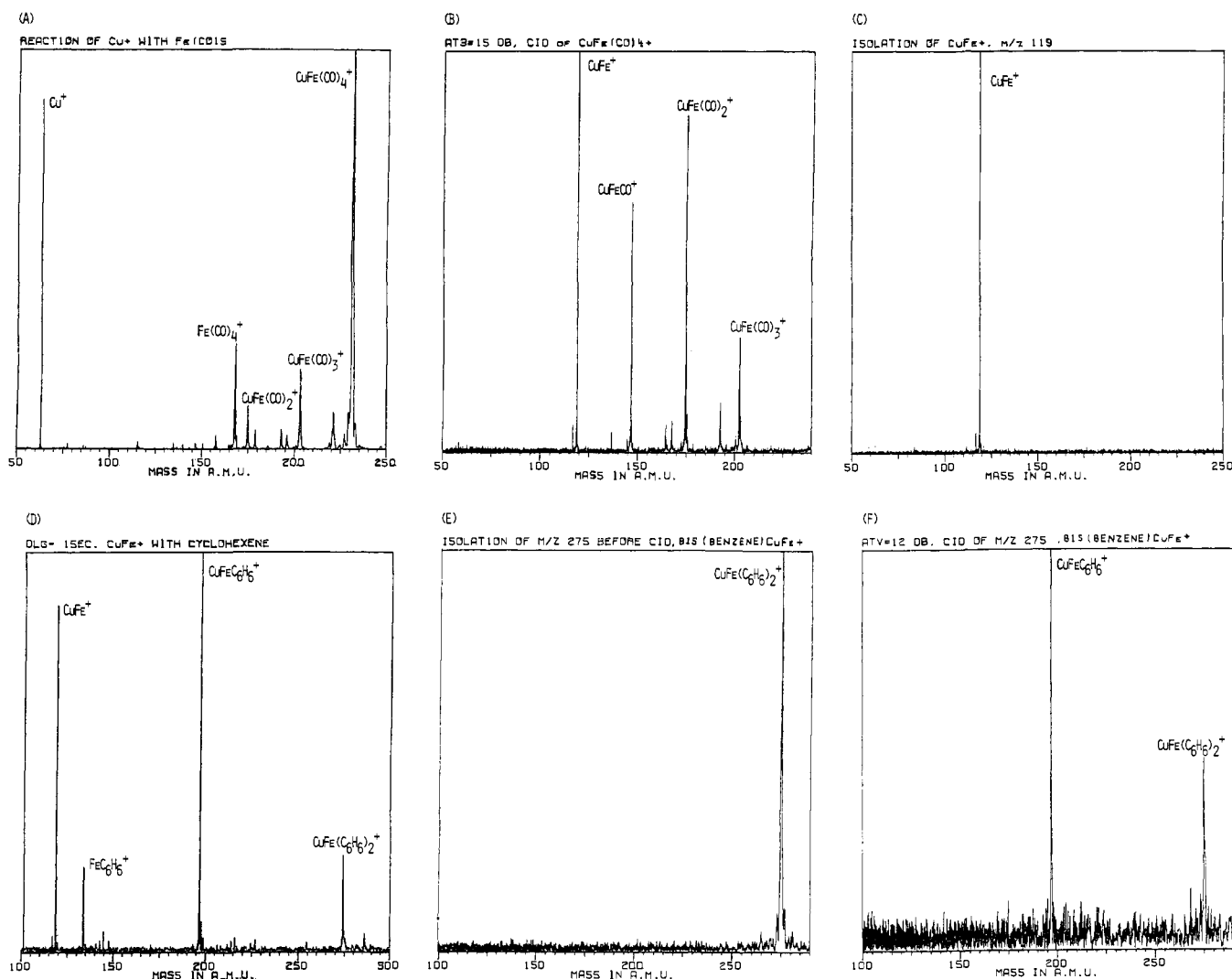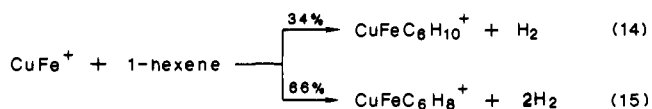
Figure 1. (A) Mass spectrum obtained from laser desorption of Cu^+ followed by isolation and reaction of $^{63}Cu^+$ with a pulse of $Fe(CO)_5$ for 350 ms in the presence of 4×10^{-6} Torr of argon. (B) Same as spectrum A except $CuFe(CO)_4^+$ is isolated, accelerated to 51 eV, and allowed to undergo collision-induced dissociation for 50 ms. (C) Same as spectrum B except all ions other than $CuFe^+$ have been ejected from the cell by swept double resonance ejection pulses. (D) Same as spectrum C except an additional 1-s trap allows $CuFe^+$ to react with cyclohexene. (E) Same as spectrum D except $CuFe(C_6H_6)_2^+$ has been isolated. (F) Same as spectrum E except $CuFe(C_6H_6)_2^+$ is accelerated to 14 eV kinetic energy with fragmentation detected. Each individual spectrum has been normalized to the most intense peak.

Reaction of $CuFe^+$ with 1-hexene yields loss of H_2 and $2H_2$, reactions 14 and 15. The secondary reactions of $CuFeC_6H_{10}^+$ and

$$CuFe^+ + \text{1-hexene} \xrightarrow{\substack{34\% \\\\ 66\%}} \begin{cases} CuFeC_6H_{10}^+ + H_2 & (14) \\\\ CuFeC_6H_8^+ + 2H_2 & (15) \end{cases}$$

$CuFeC_6H_8^+$ with 1-hexene lead to further dehydrogenation forming $CuFeC_{12}H_{18}^+$ and $CuFeC_{12}H_{16}^+$. The primary products could not be isolated easily, so only the total ratio of secondary products is reported.
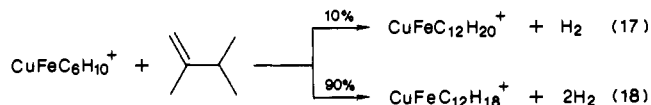
Collisional activation of $CuFeC_6H_{10}^+$ and $CuFeC_6H_8^+$ from reactions 14 and 15 produces dehydrogenation to ultimately form $CuFeC_6H_6^+$ at low energies with $CuFe^+$ observed at high energies. These results are consistent with dehydrocyclization forming $CuFe(benzene)^+$. CID of $CuFeC_{12}H_{18}^+$ and $CuFeC_{12}H_{16}^+$ is apparently inefficient and yielded no observed fragmentation over the energy range studied.

The primary reaction of $CuFe^+$ with 2,3-dimethyl-1-butene yields only H_2 elimination, forming $CuFeC_6H_{10}^+$, reaction 16.

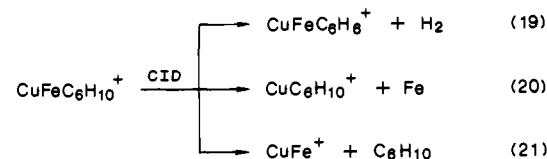$$CuFe^+ + \text{(structure)} \longrightarrow CuFeC_6H_{10}^+ + H_2 \quad (16)$$
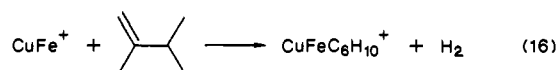
The secondary reaction of $CuFeC_6H_{10}^+$ with 2,3-dimethyl-1-butene

results in formation of $CuFeC_{12}H_{20}^+$ and $CuFeC_{12}H_{18}^+$, reactions 17 and 18. Thus, the alkadiene ligand activates the cluster complex

$$CuFeC_6H_{10}^+ + \text{(structure)} \xrightarrow{\substack{10\% \\\\ 90\%}} \begin{cases} CuFeC_{12}H_{20}^+ + H_2 & (17) \\\\ CuFeC_{12}H_{18}^+ + 2H_2 & (18) \end{cases}$$

as seen by the increase of dehydrogenation. It also appears that as the size of the reacting linear butene isomers increases, so does the ratio of $2H_2/H_2$ elimination in the secondary reactions.

CID of $CuFeC_6H_{10}^+$ from reaction 16 yields $CuFeC_6H_8^+$, $CuC_6H_{10}^+$, and $CuFe^+$, reactions 19–21. Thus, the $CuFeC_6H_{10}^+$

$$CuFeC_6H_{10}^+ \xrightarrow{CID} \begin{cases} CuFeC_6H_8^+ + H_2 & (19) \\\\ CuC_6H_{10}^+ + Fe & (20) \\\\ CuFe^+ + C_6H_{10} & (21) \end{cases}$$

isomer generated in reaction 16 is readily distinguished from the isomer generated in reaction 14 from 1-hexene. A tetramethyleneethane-bridged structure is proposed for $CuFeC_6H_8^+$ from reaction 19, structure II.

CID of $CuFeC_{12}H_{20}^+$ and $CuFeC_{12}H_{18}^+$ from reactions 17 and 18 yields sequential dehydrogenation to form $CuFeC_{12}H_{16}^+$ at low

II
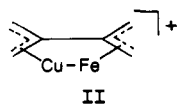
energies and CuFe⁺ at high energies. This $CuFeC_{12}H_{16}^+$ structure probably consists of two tetramethyleneethane ligands attached to CuFe⁺.

Interestingly, when CuFe⁺ reacts with 2,3-dimethyl-2-butene, elimination of H_2 is the major product forming $CuFeC_6H_{10}^+$, with some elimination of Fe neutral also observed, forming $CuC_6H_{12}^+$, reactions 22 and 23. Observation of reaction 22 implies $D°$-
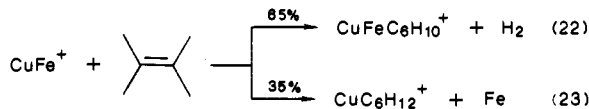

(CuFe⁺–2,3-dimethylbutadiene) > 26 kcal/mol.[25] $CuFeC_6H_{10}^+$ reacts further with 2,3-dimethyl-2-butene by eliminating H_2 and $2H_2$ to form $CuFeC_{12}H_{20}^+$ and $CuFeC_{12}H_{18}^+$, respectively. CID of both the primary and secondary cluster products yields essentially the same results as observed from the analogous ions generated from 2,3-dimethyl-1-butene, suggesting the identical structures as one would expect. For example, structure III is assigned for $CuFeC_6H_{10}^+$ generated in both reactions 16 and 22.


III
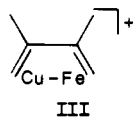
The difference between the above two compounds is the observation of reaction 23 for 2,3-dimethyl-2-butene, which implies $D°(Cu^+\text{–Fe}) \le D°(Cu^+\text{–}C_6H_{12})$, and which is not observed for 2,3-dimethyl-1-butene.

A more complex branched butene, 2,3,3-trimethyl-1-butene, reacts with CuFe⁺ to give an interesting result. The primary products consist of elimination of methane and iron, forming $CuFeC_6H_{10}^+$ and $CuC_7H_{14}^+$, respectively, reactions 24 and 25.
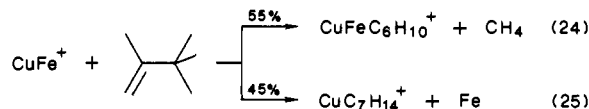

Reaction 24 probably proceeds via an initial β-methyl shift[28] from the coordinated alkene followed by β-hydride abstraction. The secondary reactions of $CuFeC_6H_{10}^+$ with 2,3,3-trimethyl-1-butene result in the multiple loss of methane and either H_2 or $2H_2$, reactions 26 and 27. These are the only examples where C–C
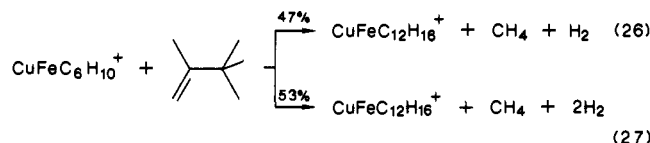
bond cleavage is observed in the reactions of CuFe⁺ with linear and branched alkenes in this study. CID of $CuFeC_6H_{10}^+$, generated from reaction 24, results in the same fragmentation as seen in reactions 19–21 suggesting structure III. CID of $CuFeC_{12}H_{18}^+$ from reaction 26 yields loss of H_2 to form $CuFeC_{12}H_{16}^+$ at low energies and only CuFe⁺ is observed at higher energies with low efficiency. These results are identical with the CID of $CuFeC_{12}H_{18}^+$ generated in reaction 18.

Cyclic C_5–C_7 Alkenes. CuFe⁺ reacts with cyclopentene by elimination of H_2 to form $CuFeC_5H_6^+$, reaction 28, implying $D°(CuFe^+\text{–cyclopentadiene}) > 24$ kcal/mol.[25] Collision-induced
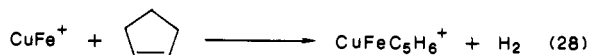
dissociation of this complex results, presumably, in the loss of CuH to form the iron cyclopentadienyl ion, exclusively, reaction 29, over the energy range studied. Interestingly, the secondary re-
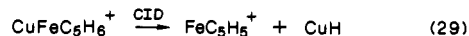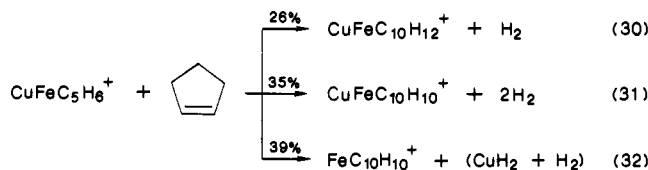

Table II. Summary of Bond Energy Limits of M⁺–L (kcal/mol) from Observed Reactions in the Text

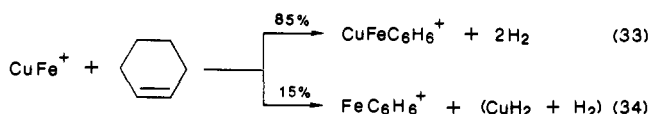|	CuFe⁺	Cu⁺	Fe⁺
CH_2	>79		
	>29	<53	<56[a]
	>26		
	>28	<53	<56
		>53	
	>26		
	>24		
	>21	≤53	≤56[b]
	>46	>53	>56
		>53	
O	>85		

[a] Reported value 48 ± 5 kcal/mol (ref 27). [b] Reported value 55 ± 5 kcal/mol (ref 27).

action of $CuFeC_5H_6^+$ with cyclopentene results in the formation of three product ions, reactions 30–32. Elimination of H_2, $2H_2$, and $(CuH_2 + H_2)$ is observed, most likely forming a bis(cyclo-

pentadiene)CuFe⁺ complex and two metallocene complexes. CID of $CuFeC_{10}H_{12}^+$ from reaction 30 yields facile elimination of H_2 to form $CuFeC_{10}H_{10}^+$. This species undergoes further CID to generate $FeC_{10}H_{10}^+$, exclusively, by loss of Cu neutral providing further evidence for metallocene structures[29] and implying $D°$-$(Fe^+\text{–}2Cp) > D°(Cu^+\text{–}2Cp)$.

The reaction of CuFe⁺ with cyclohexene yields two products: $CuFe(benzene)^+$ with elimination of $2H_2$, and $Fe(benzene)^+$ with elimination of $(CuH_2 + H_2)$, reactions 33 and 34. Observation of reaction 33 implies $D°(CuFe^+\text{–benzene}) > 21$ kcal/mol.[25] In

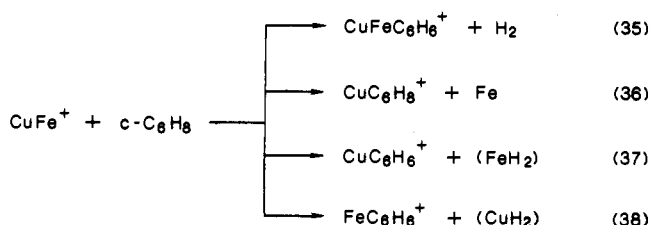order for reaction 34 to be exothermic, a CuH_2 neutral product must be invoked with $\Delta H_f(CuH_2) < 59 \pm 5$ kcal/mol and $D°$-$(Cu\text{–}H_2) > 22 \pm 5$ kcal/mol. For comparison, $\Delta H_f(FeH_2) < 77.5$ kcal/mol and $D°(Fe\text{–}H_2) > 22$ kcal/mol have been reported.[30] CID of $CuFeC_6H_6^+$ formed in reaction 33 results in facile elimination of C_6H_6 to yield CuFe⁺. This result gives a lower limit for the bond energy of CuFe⁺ which will be discussed below. Secondary reaction of $CuFeC_6H_6^+$ with cyclohexene results exclusively in the formation of a bis(benzene)CuFe⁺ complex with $2H_2$ being eliminated. CID of $CuFeC_{12}H_{12}^+$ gives elimination of C_6H_6 at low kinetic energy and elimination of $C_{12}H_{12}$ at high kinetic energy.

CuFe⁺ reacts with cyclohexadiene by dehydrogenation, as well as by breaking the metal cluster bond, reactions 35–38. The secondary reaction of $CuFeC_6H_6^+$ with cyclohexadiene results in
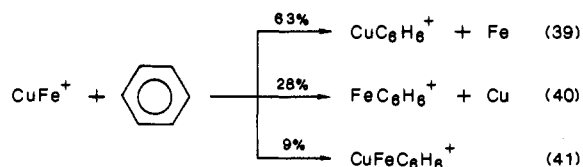
(29) Jacobson, D. B.; Freiser, B. S. *Organometallics* **1985**, *4*, 1048.
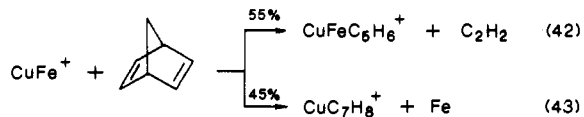(30) Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543.

$$CuFe^+ + c\text{-}C_6H_8 \longrightarrow$$

$$\longrightarrow CuFeC_6H_8^+ + H_2 \quad (35)$$

$$\longrightarrow CuC_6H_8^+ + Fe \quad (36)$$

$$\longrightarrow CuC_6H_6^+ + (FeH_2) \quad (37)$$

$$\longrightarrow FeC_6H_6^+ + (CuH_2) \quad (38)$$

elimination of Fe and CuH_2 yielding $CuC_{12}H_{14}^+$ and $FeC_{12}H_{12}^+$, respectively, which is surprisingly different from the secondary reaction of $CuFeC_6H_6^+$ with cyclohexene where only a bis-(benzene)$CuFe^+$ complex is observed.

The reaction of $CuFe^+$ with benzene yields another interesting result. The metal cluster bond breaks and both $FeC_6H_6^+$ and $CuC_6H_6^+$ are observed as well as some condensation product, reactions 39–41. These reactions give an upper limit for the bond energy of $CuFe^+$ as discussed below.
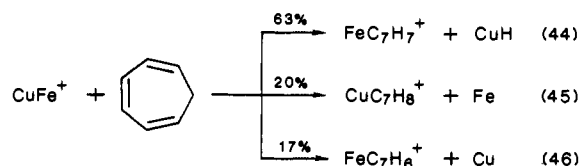
$$CuFe^+ + \langle\bigcirc\rangle \longrightarrow$$

$$\xrightarrow{63\%} CuC_6H_6^+ + Fe \quad (39)$$

$$\xrightarrow{28\%} FeC_6H_6^+ + Cu \quad (40)$$

$$\xrightarrow{9\%} CuFeC_6H_6^+ \quad (41)$$

Practically the same ratio of Fe/Cu elimination is observed when $CuFe^+$ is allowed to react with toluene, as compared to the reaction of $CuFe^+$ with benzene, with no other products observed. The CuFe(toluene)$^+$ complex can be generated from the reaction of $CuFe^+$ with 3-methylcyclohexene. CID of this complex, $CuFeC_7H_8^+$, yields elimination of Fe at low energies to give $CuC_7H_8^+$ with small amounts of $CuFe^+$ also observed at high energies.

In contrast, the reaction of $CuFe^+$ with norbornadiene is the only other instance where C–C cleavage is observed in this data set. The primary reaction yields C_2H_2 elimination and Fe elimination, reactions 42 and 43. This chemistry is clearly quite
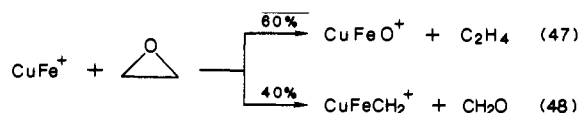
$$CuFe^+ + \text{(norbornadiene)} \longrightarrow$$

$$\xrightarrow{55\%} CuFeC_6H_6^+ + C_2H_2 \quad (42)$$

$$\xrightarrow{45\%} CuC_7H_8^+ + Fe \quad (43)$$

different than that observed for toluene. Collision-induced dissociation of the $CuFeC_5H_6^+$ complex formed in reaction 42 yields solely elimination of CuH, leaving $FeC_5H_5^+$ as the observed product. This observation indicates a cyclopentadiene ring bound to the $CuFe^+$ metal cluster as expected for a retro-Diels–Alder process. The secondary reaction of $CuFeC_5H_6^+$ with norbornadiene yields only the displacement of Cu, generating $FeC_{12}H_{14}^+$.

$CuFe^+$ reacts with cycloheptene to eliminate $2H_2$, generating $CuFeC_7H_8^+$, exclusively. This observation implies D°($CuFe^+$–cycloheptatriene) > 46 kcal/mol.[25] Collision-induced dissociation of $CuFeC_7H_8^+$ eliminates CuH, leaving $FeC_7H_7^+$, exclusively. This observation is quite different from the CID results of CuFe(toluene)$^+$ implying different structures. $FeC_7H_7^+$ is also observed when $CuFe^+$ is allowed to react with cycloheptatriene, reactions 44–46.

$$CuFe^+ + \text{(cycloheptatriene)} \longrightarrow$$

$$\xrightarrow{63\%} FeC_7H_7^+ + CuH \quad (44)$$

$$\xrightarrow{20\%} CuC_7H_8^+ + Fe \quad (45)$$

$$\xrightarrow{17\%} FeC_7H_8^+ + Cu \quad (46)$$

Reactions with Oxygenated Compounds. The oxide chemistry of selected bare dimer and trimer ions has recently been reported.[13,31] Reaction of $CuFe^+$ with ethylene oxide yields $CuFeO^+$ and $CuFeCH_2^+$ by eliminating C_2H_4 and CH_2O, respectively,

reactions 47 and 48. Collision-induced dissociation of $CuFeO^+$

$$CuFe^+ + \text{(ethylene oxide)} \longrightarrow$$

$$\xrightarrow{60\%} CuFeO^+ + C_2H_4 \quad (47)$$

$$\xrightarrow{40\%} CuFeCH_2^+ + CH_2O \quad (48)$$

generates FeO and Cu^+, exclusively. Observation of reaction 47 implies D°($CuFe^+$–O) > 85 kcal/mol.[25] Observation of reaction 48 implies D°($CuFe^+$–CH_2) > 79 kcal/mol.[25] In contrast, Fe^+ reacts with ethylene oxide to generate $FeCH_2^+$ and $FeCO^+$ with neutral losses of CH_2O and CH_4, respectively.

Reaction of $CuFe^+$ with O_2 yields Cu^+ exclusively, with presumably FeO_2 being eliminated, reaction 49. D°(Fe–2O) has been

$$CuFe^+ + O_2 \longrightarrow Cu^+ + FeO_2 \quad (49)$$
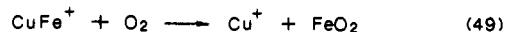
reported as >185 ± 7 kcal/mol[31] which gives ΔH_f(FeO_2) < 33 ± 7 kcal/mol.[25]

$CuFe^+$ is unreactive with N_2O as is VFe^{+12} and $CoFe^{+31}$ despite the weak N_2–O bond. Absence of reaction may imply a kinetic barrier.[32]

Reactivity Comparison of CoFe$^+$ and VFe$^+$. All three heteronuclear cluster ions do not react with linear (C_1–C_6) nor cyclic (C_3–C_6) alkanes.[12,13] While $CuFe^+$ and $CoFe^+$ are first-row late–late transition-metal heteronuclear cluster ions, VFe^+ is an early–late first-row transition-metal cluster ion. Therefore, one might expect similar reactivity between $CuFe^+$ and $CoFe^+$ and quite different reactivity between $CuFe^+$ and VFe^+, as seems to be the case here.

$CuFe^+$ reacts very similarly to $CoFe^+$ with (C_4–C_7) alkenes.[12] The major difference is that in the secondary reactions of $CoFe^+$ with a few of the alkenes, somewhat more multiple dehydrogenation is observed.[11] For example, both $CuFe^+$ and $CoFe^+$ react with the linear butenes to generate products due to H_2 loss. These products, $MFeC_4H_6^+$ (M = Co, Cu), react further with the linear butenes to generate products corresponding to an additional loss of H_2, i.e., $MFeC_8H_{12}^+$ (M = Co, Cu). However, the reactions of $CoFeC_4H_6^+$ with the linear butenes also generate ~40% of $CoFeC_8H_{10}^{+}$.[12]

Reactions of $CoFe^+$ with oxygenated compounds are also slightly different than those with $CuFe^+$, with $CoFe^+$ being more reactive.[31] For example, $CoFe^+$ abstracts up to two oxygen atoms from ethylene oxide while $CuFe^+$ only abstracts one oxygen atom. Also, $CoFe^+$ will abstract an oxygen atom from oxygen while $CuFe^+$ only reacts to form Cu^+ and FeO_2.

In contrast, the reactivity of VFe^+ is quite different than that of either $CuFe^+$ or $CoFe^+$. VFe^+ is completely unreactive with linear (C_2–C_6) alkenes.[13] However, VFe^+ does react with both cyclohexene and benzene to produce $VFeC_6H_6^+$ and $VFeC_{12}H_{12}^+$.[13] CID of $VFeC_{12}H_{12}^+$ yields exclusively $VC_{12}H_{12}^{+13}$ while CID of $CuFeC_{12}H_{12}^+$ from the reaction with cyclohexene yields $CuFeC_6H_6^+$ with no breakage of the cluster bond. VFe^+ also reacts slowly with cycloheptene to lose $2H_2$ and form $VFeC_7H_8^{+}$.[13] However, carbene abstraction results from the reaction of VFe^+ with cycloheptatriene[13] compared to cleavage of the $CuFe^+$ bond, reactions 44–46. VFe^+ also abstracts up to three oxygen atoms from ethylene oxide and reacts with oxygen to form VO^+ and Fe^+ with loss of FeO and VO_2 neutrals, respectively.[13]

Bond Energies and Related Thermochemistry. The reactions of $CuFe^+$ with butadiene yields a lower limit for D°(Cu^+–Fe). Since no reaction is observed, D°(Cu^+–Fe) > D°(Cu^+–C_4H_6) and D°(Fe^+–Cu) > D°(Fe^+–C_4H_6) = 48 ± 5 kcal/mol are suggested.[27] Another result comes from the CID of $CuFeC_6H_6^+$ formed in reaction 33 between $CuFe^+$ and cyclohexene which yields exclusive loss of C_6H_6 and implies D°(Cu^+–Fe) > D°(Cu^+–benzene) and D°(Fe^+–Cu) > D°(Fe^+–benzene) = 55 ± 5 kcal/mol.[27]

In the reaction of $CuFe^+$ with benzene, however, both Cu(benzene)$^+$ and Fe(benzene)$^+$ are observed, reactions 39 and 40. This observation implies D°(Cu^+–Fe) < D°(Cu^+–benzene) and

(31) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 27.

(32) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2449.

Reactions of CuFe+ with Hydrocarbons

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$D°(Fe^+-Cu) < D°(Fe^+-benzene) = 55 \pm 5$ kcal/mol.[27] The apparent discrepancy between these results and the CID of $CuFeC_6H_6^+$ from reaction 33 can be rationalized. The reaction between $CuFe^+$ and benzene, reactions 39–41, was measured to be about 10% of the Langevin rate ($\sim 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) which could imply a slightly endothermic reaction since only exothermic or slightly endothermic reactions are observed under normal conditions in FTMS. Thus, assuming reaction 40 is slightly endothermic suggests $D°(Fe^+-Cu)$ is only a few kcal/mol greater than $D°(Fe^+-benzene)$, implying $D°(Fe^+-Cu) = 58 \pm 9$ kcal/mol. From this result and from the difference in the ionization potentials of Cu and Fe,[33] $D°(Cu^+-Fe) = 55 \pm 9$ kcal/mol is calculated. This latter value falls well within the limits discussed above. Finally, in an independent study, photodissociation of $CuFe^+$ gave $D°(Cu^+-Fe) = 53 \pm 7$ kcal/mol and $D°(Fe^+-Cu) = 56 \pm 7$ kcal/mol,[34] which is in excellent agreement with this work.

From $D°(Cu^+-Fe)$, $\Delta H_f(CuFe^+) = 305 \pm 7$ kcal/mol has been calculated.[25] For comparison, $D°(Fe^+-Fe) = 63.5 \pm 6$ kcal/mol, $D°(Co^+-Fe) = 66 \pm 7$ kcal/mol,[11a] and $D°(V^+-Fe) = 75 \pm 5$ kcal/mol.[13]

With these bond energies determined, observation of reaction 43 from $CuFe^+$ and norbornadiene implies $D°(Cu^+-C_7H_8) > 53 \pm 7$ kcal/mol and observation of reactions 45 and 46 from $CuFe^+$ and cycloheptatriene yields $D°(Cu^+-C_7H_8) > 53 \pm 7$ kcal/mol and $D°(Fe^+-C_7H_8) > 56 \pm 7$ kcal/mol, respectively.[25]

A theoretical Cu–Fe bond energy of 30 kcal/mol has been reported.[35] Using this value and the value assigned above for $D°(Cu^+-Fe)$ in eq 50 yields a calculated IP(CuFe) = 6.7 eV.

$$IP(CuFe) = D°(Cu-Fe) + IP(Cu) - D°(Cu^+-Fe) \qquad (50)$$

Again for comparison, IP(Fe$_2$) = 5.90 eV,[36] IP(CoFe) = 6.34 eV,[11a] and IP(VFe) = 5.40 eV.[13] Finally, collision-induced dissociation of $CuFe^+$ yields both Cu^+ and Fe^+ with Cu^+ more abundant until high kinetic energies (~ 90 eV, lab), where the intensities of Cu^+ and Fe^+ become approximately equal which is consistent with the similar IPs of Cu and Fe.

The weaker bond energy of $CuFe^+$ and the higher IP of CuFe suggest that the bonding between the d orbitals may not play an important role in the bonding of the cluster. These characteristics have also been observed for $CoFe^+$ where the bonding has been postulated to be almost entirely due to the 4s molecular orbitals.[12] In contrast, it has been postulated that the d electrons in VFe^+ might participate in the bonding process due to the low IP of VFe and the strong bond energy of VFe^+.[13] However, detailed theoretical calculations and spectroscopic measurements must be done to completely understand this bonding.

Conclusions

The reactivity of $CuFe^+$ differs greatly from the corresponding atomic metal ions, Cu^+ and Fe^+. $CuFe^+$ is unreactive with alkanes even though Fe^+ reacts with them via C–H and C–C insertions.[23] This reactivity is consistent with that observed for $CoFe^+$[12] and VFe^+.[13] $CuFe^+$ reacts with aliphatic alkenes which contain a linear C_4 unit, yielding predominantly dehydrogenation. The only C–C cleavage observed is in the reactions of $CuFe^+$ with 2,3,3-trimethyl-1-butene and norbornadiene where a β-methyl abstraction and a retro-Diels–Alder reaction occur, eliminating methane and acetylene, respectively.

The reactions of $CuFe^+$ with benzene, butadiene, and O_2 along with the results of the CID of $CuFeC_6H_6^+$ generated from cyclohexene are consistent with photodissociation results[34] yielding $D°(Fe^+-Cu) = 56 \pm 7$ kcal/mol, $D°(Cu^+-Fe) = 53 \pm 7$ kcal/mol, IP(CuFe) = 6.7 eV, and $\Delta H_f(CuFe^+) = 305 \pm 7$ kcal/mol.

Upon examination of Table I, the secondary reactions typically indicate more dehydrogenation than the primary reactions. The addition of an alkadiene ligand apparently activates the cluster for dehydrogenation. This trend is also observed with the reactions of $CoFe^+$ with alkenes.[12]

The reactions of $CuFe^+$ are very similar to those of $CoFe^+$. The studies of other heteronuclear cluster ions are currently underway in an effort to understand the differences and similarities in reactivity.

(33) IPs of Cu and Fe taken from the following: Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 59th ed.; CRC Press, Inc.: Cleveland, 1978.

(34) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

(35) Weltner, W., Jr.; Van Zee, R. J. *Annu. Rev. Phys. Chem.* **1984**, *35*, 291.

(36) Lin, S-S.; Kant, A. *J. Phys. Chem.* **1969**, *73*, 2450.