

Infrared Multiphoton Dissociation of $MC_4H_6^+$ [M = Fe, Co, or Ni; $C_4H_6 = 1,3$ -Butadiene or $(C_2H_2)(C_2H_4)$]

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Abstract: The infrared multiphoton dissociation (IRMPD) of the two isomers, $M(1,3$ -butadiene)⁺ and $M(C_2H_2)(C_2H_4)^+$ (M = Fe, Co, or Ni), was investigated. For the butadiene system, $FeC_4H_6^+$ was observed to give three products, $CoC_4H_6^+$ four products, and $NiC_4H_6^+$ only one product. The observation of four products has not been previously seen in IRMPD studies of ions and suggests a fortuitous balance of several factors. Interestingly, the IRMPD of $M(\text{butadiene-}1,1,4,4\text{-}d_4)^+$ was observed not only to give one product for M = Fe, Co, or Ni but also to proceed with a decreased photodissociation rate. For the $M(C_2H_2)(C_2H_4)^+$ system, IRMPD suggests that $D^\circ(Co^+-C_2H_2) \sim D^\circ(Co^+-C_2H_4)$. Also, SORI and/or competitive CID indicate that $D^\circ(M^+-C_2H_2) > D^\circ(M^+-C_2H_4)$ by 0.5–2 kcal/mol for M = Fe or Ni. On the basis of these observations, we assign $D^\circ(Fe^+-C_2H_2) = 36 \pm 2$ kcal/mol, $D^\circ(Co^+-C_2H_2) = 43 \pm 2$ kcal/mol, and $D^\circ(Ni^+-C_2H_2) = 45 \pm 2$ kcal/mol. These results are compared to recent theoretical and experimental findings.

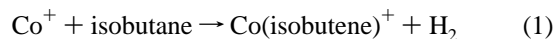
Introduction

Infrared multiphoton dissociation (IRMPD) represents one of the arsenal of techniques to probe molecular phenomena associated with gas-phase ions, such as unimolecular and bimolecular reaction dynamics,^{1,2} vibrational relaxation,³ photoinduced reactions,^{4,5} and isotopic and isomeric selectivity.^{6–8} While this method has been applied successfully to many organic ion structures,^{5,9–15} surprisingly few papers have appeared dealing with metal-containing ions.^{4,6,16–19} This study extends the use of the infrared multiphoton experiment to investigate the fragmentation characteristics of groups 8–10 (Fe, Co, or Ni) C_4H_6 [1,3-butadiene (**I**) and $(C_2H_2)(C_2H_4)$ (**II**)] ion complexes.



The interest in studying the IRMPD of $MC_4H_6^+$ (**I**) came as a result of a photodissociation study on $CoC_4H_8^+$ isomers.¹⁹ In

that study, $CoC_4H_8^+$ from the reaction of Co^+ with isobutane, reaction 1, underwent infrared activation to produce $CoC_4H_6^+$



as one of several photoproducts which, based on previous work not involving IRMPD, was believed to be $Co(1,3$ -butadiene)⁺.^{20,21} Continuous ejection of $CoC_4H_6^+$ resulted in the disappearance of $CoC_4H_4^+$ and $CoC_2H_2^+$ and in the decrease of Co^+ intensity, indicating that $CoC_4H_6^+$ undergoes photodissociation to produce these three product ions. Since multiple products are not common for IRMPD,^{4,6,22,23} an investigation of $M(1,3$ -butadiene)⁺ (M = Fe, Co, or Ni) was carried out.

The purpose in studying the IRMPD of $M(C_2H_2)(C_2H_4)^+$ (**II**) was twofold: to look for competitive ligand loss as a means of determining relative and absolute metal–ligand bond strengths in a manner analogous to collision-induced dissociation (CID) methods^{24–26} and to complement 1,3-butadiene as an isomer of $MC_4H_6^+$. In a previous study, equal loss of acetone and acetone-*d*₆ from the IRMPD of $M(\text{acetone})(\text{acetone-}d_6)^+$ (M = Fe, Co) indicated that the bond strengths of M^+ –acetone and M^+ –acetone-*d*₆ are comparable, which is fully expected, since

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the binding is through the oxygen by electrostatic interaction.^{6,27} In contrast, IRMPD of $\text{Co}(\text{C}_2\text{H}_4)(\text{C}_3\text{H}_6)^+$ (**III**) yields exclusive



III

loss of C_2H_4 , indicating that C_3H_6 is bound more strongly than C_2H_4 to the metal center.¹⁹ The difference in the bond strengths cannot exceed ~ 3 kcal/mol, however, as evidenced by the successful displacement of propene from MC_3H_6^+ ($\text{M} = \text{Fe}, \text{Co}, \text{or Ni}$) by perdeuterated ethene, reaction 2.²⁸ These results



can be compared to those of Beauchamp and Bowers, who reported $D^\circ(\text{Co}^+ - \text{C}_2\text{H}_4) = 42 \pm 5$ kcal/mol^{29a} and $D^\circ(\text{Co}^+ - \text{C}_3\text{H}_6) = 44 \pm 3$ kcal/mol,^{29b} and to more recent values of $D^\circ(\text{Co}^+ - \text{C}_2\text{H}_4) = 42.9 \pm 1.6$ kcal/mol and $D^\circ(\text{Co}^+ - \text{C}_3\text{H}_6) = 43.1 \pm 1.6$ kcal/mol,^{30a} reported by Armentrout and co-workers.

While values for $D^\circ(\text{M}^+ - \text{C}_2\text{H}_2)$ are widely available for $\text{M} =$ early transition metals,^{31–34} the only experimental energies reported in the literature for the late transition metals are $D^\circ(\text{Fe}^+ - \text{C}_2\text{H}_2) = 32 \pm 6$ kcal/mol^{30d} and $D^\circ(\text{Co}^+ - \text{C}_2\text{H}_2) = 39.7$ kcal/mol.^{30a–c} These results can be compared to theoretical predictions at 0 K of 28, 37, 39, and 36 kcal/mol for $\text{M} = \text{Fe}, \text{Co}, \text{Ni},$ and Cu , respectively, calculated by Bauschlicher and co-workers.³¹ In this study, we obtain additional information on $D^\circ(\text{M}^+ - \text{C}_2\text{H}_2)$ based on IRMPD and/or collision-induced dissociation results and reported values of $D^\circ(\text{M}^+ - \text{C}_2\text{H}_4)$.

Sustained off-resonance irradiation (SORI), a collisional activation technique designed by Jacobson and co-workers to mimic infrared activation,³⁵ was also performed on the ions investigated in this paper. The results from this work support the similarity of these two methods.

Experimental Section

Experiments were performed on a Nicolet FTMS-2000 Fourier transform ion cyclotron resonance (FTICR) mass spectrometer.^{36,37} This instrument features a dual cubic cell (4.9 cm on each edge) that permits

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ion transfer between the source cell and the analyzer cell.^{38,39} The cell is situated in the bore of a 3.0 T superconducting magnet. The metal ions were generated by laser desorption using the fundamental beam of a Quanta Ray Nd:YAG laser (1.06 μm) focused onto the metal target.⁴⁰ After their formation, the metal ions were cooled in the source cell by collisions with argon at $\sim 1 \times 10^{-6}$ Torr for 2 s in an effort to remove excess electronic and kinetic energy.^{41,42} While the presence of a small population of excited ions cannot be completely ruled out,⁴¹ it is not expected to significantly affect the IRMPD results. 1,3-Butadiene-1,1,4,4-*d*₄ (98% pure) was obtained from Cambridge Isotope Laboratories. Its isotopic purity was checked in our laboratory by reacting it with Ni^+ , which was chosen because Ni^+ reacts with 1,3-butadiene to yield the condensation product, exclusively, whereas Co^+ and Fe^+ yield several products (*vide infra*). The Ni^+ reaction produced 97.5% $\text{NiC}_4\text{H}_2\text{D}_4^+$ and 2.5% $\text{NiC}_4\text{H}_3\text{D}_3^+$.

After the parent ions were isolated in the source side, they were irradiated with a Synrad 48-2-115 continuous-wave CO_2 laser at a wavelength of 10.6 μm (944 cm^{-1}). The beam diameter of the CO_2 laser (fwhm) at a distance of 318 cm (i.e., the distance between the laser aperture and the cell) was measured to be 7.1 mm. While the photodissociation yield, defined as the photoproduct ion intensity divided by the total ion intensity at time t , was observed to decrease with lower laser power and shorter irradiation time, the ratio of product ions was observed to be independent of both the laser power (5–27 W) and the irradiation time (0.5–6 s). A Uniblitz mechanical shutter model VS25S2W0 was used to gate the infrared laser. The shutter opening time was approximately 5 ms. An uncalibrated Coherent model 201 power meter was used to monitor the nominal power of the CO_2 laser. A ZnSe window was used to allow the unfocused infrared laser beam to enter the vacuum enclosure. Since argon was used to cool the metal ions, it was convenient to also have it present during infrared irradiation. Even though the effect of the argon was usually a decrease in the photodissociation yield,¹⁰ its presence was observed not to change the ratio of photoproducts when multiple products were formed.

Collision-induced dissociation was performed using argon as the collision gas at a pressure of $\sim (1-2) \times 10^{-6}$ Torr.⁴³ The collision energy of the ions was varied between 0 and 45 eV (reported as laboratory collision energy). For the SORI experiments,³⁵ argon [$\sim (1-2) \times 10^{-6}$ Torr] was also used as the collision gas. The translational energy given to the ions when exciting them with an “off-resonance” electric field pulse is given by

$$E_{\text{tr}} = \{E^2 e^2 / [4m(\omega_1 - \omega_c)^2]\} [\sin^2(\omega_1 - \omega_c)(t/2)]$$

where ω_1 is the excitation frequency and ω_c is the natural cyclotron frequency. Thus, E_{tr} is an oscillating function which, in physical terms, means that the ions undergo acceleration–deceleration cycles during the electric field pulse. The maximum kinetic energy in these cycles occurs when the \sin^2 term is equal to 1, yielding

$$E_{\text{tr,max}} = E^2 e^2 / [4m(\omega_1 - \omega_c)^2]$$

which depends on the amplitude of the applied electric field, E , the mass of the ion, m , and the frequency difference, $\omega_1 - \omega_c$. Unlike conventional CID, however, in which the maximum energy varies with t^2 , the maximum SORI energy is independent of irradiation time. In the experiments in this work, $\omega_1 - \omega_c = 2$ kHz was kept constant and the electric field values were varied from about 0.42 to 0.67 V/cm peak-to-peak, yielding $E_{\text{tr,max}}$ energies of between about 2.5 and 6.2 eV, depending on the ion involved.

In principle, optimum SORI conditions are those in which the ions experience the smallest increment of internal energy change per collision prior to dissociation. In practice, as the energy is reduced, the number

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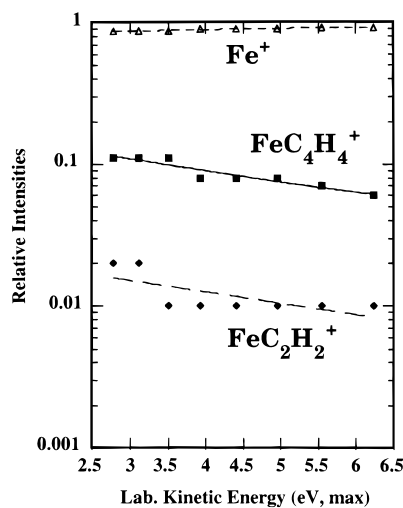


Figure 1. SORI of $FeC_4H_6^+$, generated from reaction 3.

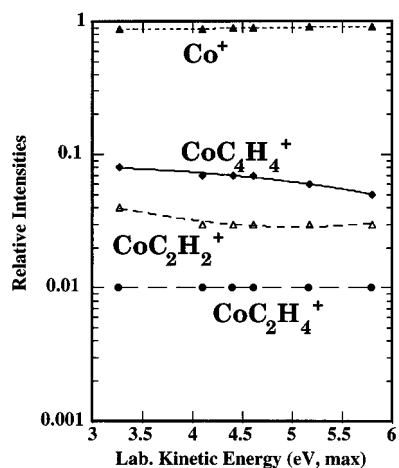
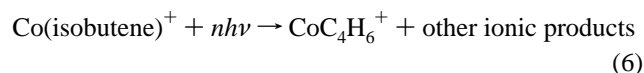


Figure 2. SORI of $CoC_4H_6^+$, generated from reaction 3.

and ratio of the products remain essentially constant until poor signal prevents any further reduction in collision energy.¹⁹ Thus, for the SORI data plotted in Figures 1 and 2, the product ratios do not change substantially down to about 3 eV, below which SORI signals were no longer observed.

Results

$M(1,3\text{-butadiene})^+$. $M(1,3\text{-butadiene})^+$ ($M = Fe, Co, \text{ or } Ni$) was prepared from the reaction of M^+ with 1-butene, reaction 3.^{21,44} In addition, $CoC_4H_6^+$, prepared by (i) displacement of propene from $CoC_3H_6^+$ by butadiene, reactions 4 and 5, and (ii) as a photoproduct of $Co(\text{isobutene})^+$, reaction 6, gave identical results to $CoC_4H_6^+$ generated in reaction 3, within experimental error. IRMPD of $MC_4H_6^+$ yields loss of H_2 , C_2H_4 , and C_4H_6 for iron, loss of H_2 , C_2H_2 , C_2H_4 , and C_4H_6 for cobalt, and loss of C_4H_6 , exclusively, for nickel (Table 1).



In order to probe the dissociation mechanism, $M(\text{butadiene-}1,1,4,4\text{-}d_4)^+$ was also prepared and photodissociated. In addition,

Table 1. IRMPD of $MC_4H_6^+$ ($M = Fe, Co, Ni$)

M^+	neutral loss, %				condition	photodissociation yield
	H_2	C_2H_2	C_2H_4	C_4H_6		
Fe	28		4	68	2 s, 27 w	0.53
Co	23	5	13	59	3 s, 27 w	0.87
Ni				100	1 s, 22 w	0.76

Table 2. IRMPD of $M(\text{butadiene-}1,1,4,4\text{-}d_4)^+$ ($M = Fe, Co, Ni$)

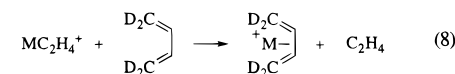
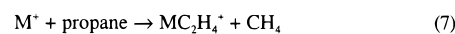
$$M^+ + \begin{array}{c} D_2C \\ | \\ C=C \\ | \\ D_2C \end{array} + nh\nu \rightarrow M^+ + \begin{array}{c} D_2C \\ | \\ C=C \\ | \\ D_2C \end{array}$$

metal	condition	photodissociation yield ^a
Fe	6 s, 27 W	0.53
Co	5 s, 27 W	0.50
Ni	6 s, 27 W	0.50

^a Note that all of the yields are lower than those in Table 1, considering the longer irradiation times involved.

tion, SORI and conventional CID of $M(\text{butadiene})^+$ and $M(\text{butadiene-}1,1,4,4\text{-}d_4)^+$ were performed, and the primary reactions of M^+ with butadiene and with butadiene- $1,1,4,4\text{-}d_4$ were investigated.

$M(\text{butadiene-}1,1,4,4\text{-}d_4)^+$ for $M = Fe$ or Ni was prepared by ligand displacement, reactions 7 and 8:



($M = Fe, Ni$)

For $M = Co$, n -butane was used instead of propane because it generated a greater abundance of $CoC_2H_4^+$.⁴³ Also, even though butadiene- $1,1,4,4\text{-}d_4$ displaces propene from $Co(\text{propene})^+$, as in reactions 4 and 5, H/D exchanges prevented the generation of $Co(\text{butadiene-}1,1,4,4\text{-}d_4)^+$ in good abundance by this route.²¹ With $M(C_2H_4)^+$, however, exchange did not occur or occurred only to a minimal extent (<5%).

In contrast to the results on $MC_4H_6^+$ for $M = Fe$ or Co , infrared activation of the deuterated species results in loss of the whole ligand, exclusively. From Tables 1 and 2, it can also be seen that the undeuterated complex photodissociates more readily than the deuterated species. In general, there are two ways of comparing the relative photodissociation cross sections of two ions: (1) by comparing the yield for the ions taken under the same conditions and (2) by having both ions present at the same time so that they can be irradiated simultaneously.^{6,7} Often, there are neighboring ions that have frequencies that are close to the ion of interest. In these cases, caution must be exercised in performing method 1, since the ejection of the neighboring ions may result indirectly in the increase in internal energy of the parent ion which, in turn, increases photodissociation yield. To rule out this possibility, method 2 was also undertaken. In this instance, $MC_2H_4^+$ was allowed to react with a mixture of regular and deuterated butadiene, and the parent ions, $M(\text{butadiene})^+$ and $M(\text{butadiene-}1,1,4,4\text{-}d_4)^+$, were irradiated simultaneously. Figure 3, for example, provides clear evidence that, indeed, the undeuterated $Co(\text{butadiene})^+$ complex photodissociates more readily than the deuterated species. The same was found to be true for the iron and nickel analogues.

CID of regular and deuterated $M(\text{butadiene})^+$ yields loss of the whole ligand, exclusively, over the energy range studied. The results for $M(\text{butadiene})^+$ are in excellent agreement with the previous studies.⁴⁴ For SORI, the results for undeuterated

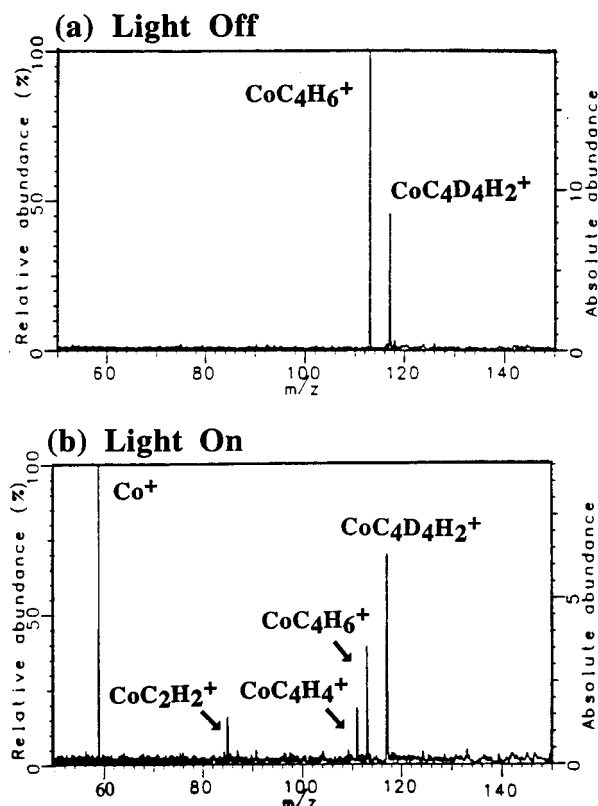


Figure 3. IRMPD of a mixture of $\text{Co}(\text{butadiene})^+$ and $\text{Co}(\text{butadiene-1,1,4,4-d}_4)^+$, showing the rate of dissociation for the undeuterated species is faster than that of deuterated species. Conditions of the experiment: time of irradiation of infrared light is 5 s, power is 27 W. (a) Light off, spectrum before irradiation. (b) Light on, spectrum after irradiation.

Table 3. SORI of $\text{M}(\text{butadiene})^+$ ($\text{M} = \text{Fe, Co, Ni}$)

M^+	neutral loss, %				energy (lab), eV (max)
	H_2	C_2H_2	C_2H_4	C_4H_6	
Fe	11		2	87	2.8
Co	8	1	4	87	3.3
Ni				100	at all energies (3.5–8.7)

Table 4. Primary Reactions of M^+ ($\text{M} = \text{Fe, Co, Ni}$) with 1,3-Butadiene^a

	Fe, %	Co, %	Ni, %
$\text{M}^+ + 1,3\text{-butadiene} \rightarrow \text{MC}_4\text{H}_6^+$	42	52	100
$\text{MC}_4\text{H}_4^+ + \text{H}_2$	50	29	
$\text{MC}_2\text{H}_4^+ + \text{C}_2\text{H}_2$		5	
$\text{MC}_2\text{H}_2^+ + \text{C}_2\text{H}_4$	8	14	

^a Butadiene and argon were leaked into the cell at $\sim 8 \times 10^{-8}$ and 2.6×10^{-6} Torr, respectively. The metal ions were cooled for 2 s and then reacted with butadienes for 0.1–0.4 s to give observable products.

and deuterated $\text{M}(\text{butadiene})^+$ were similar to the IRMPD results with the exception that SORI tends to produce the direct cleavage product, loss of the whole ligand, in greater abundance (Table 3). The SORI energy profiles for FeC_4H_6^+ and CoC_4H_6^+ are shown in Figures 1 and 2.

The primary reactions of M^+ with undeuterated and deuterated butadiene yield loss of hydrogen and other products for $\text{M} = \text{Fe}$ and Co with extensive scrambling observed with deuterated butadiene. However, only a condensation product was observed for $\text{M} = \text{Ni}$ (Tables 4 and 5). The reactions of nonthermalized Fe^+ and Ni^+ with regular butadiene yielded additional products that were not observed when these ions were collisionally cooled. In these instances, FeC_2H_4^+ , NiC_2H_2^+ , and

Table 5. Primary Reactions of M^+ ($\text{M} = \text{Fe, Co, Ni}$) with butadiene-1,1,4,4-d₄^a

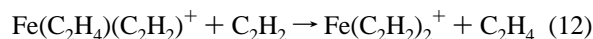
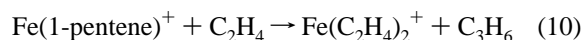
	Fe, %	Co, %	Ni, %
$\text{M}^+ + 1,3\text{-butadiene } 1,1,4,4\text{-d}_4 \rightarrow$			
$\text{MC}_4\text{H}_2\text{D}_4^+$	80	80	100
$\text{MC}_4\text{D}_4^+ + \text{H}_2$	3	2	
$\text{MC}_4\text{HD}_3^+ + \text{HD}$	8	4	
$\text{MC}_4\text{H}_2\text{D}_2^+ + \text{D}_2$	3	2	
$\text{M}(\text{D}_2\text{C}=\text{CD}_2)^+ + \text{C}_3\text{H}_2$		1	
$\text{M}(\text{D}_2\text{C}=\text{CHD})^+ + \text{C}_2\text{HD}$		3	
$\text{M}(\text{DHC}=\text{CHD})^+ + \text{C}_2\text{D}_2$		1	
$\text{M}(\text{DC}=\text{CD})^+ + \text{C}_2\text{H}_2\text{D}_2$	2	2	
$\text{M}(\text{DC}=\text{CH})^+ + \text{C}_2\text{HD}_3$	4	4	
$\text{M}(\text{HC}=\text{CH})^+ + \text{C}_2\text{D}_4$		1	

^a Butadiene and argon were leaked into the cell at $\sim 8 \times 10^{-8}$ and 2.6×10^{-6} Torr, respectively. The metal ions were cooled for 2 s and then reacted with butadienes for 0.1–0.4 s to give observable products.

NiC_2H_4^+ were observed (about 3%, 4%, and 8%, respectively). These results suggest that the activation barriers associated with these products are above the M^+ –butadiene dissociation limit. NiC_4H_4^+ , however, was not observed in the reaction of hot Ni^+ with butadiene, suggesting that the activation barrier for its formation is above that of NiC_2H_2^+ and NiC_2H_4^+ and/or this product is kinetically unfavored. With cobalt, since CoC_2H_2^+ , CoC_2H_4^+ , and CoC_4H_4^+ were already formed as a result of thermal reactions, the effect of hot ions was less dramatic.

MC_4H_4^+ ($\text{M} = \text{Fe, Co}$), generated by SORI on MC_4H_6^+ , were studied by CID and SORI. Loss of the whole ligand was observed at all CID and SORI energies for both ions.

$\text{M}(\text{C}_2\text{H}_2)(\text{C}_2\text{H}_4)^+$. As previously reported, FeC_4H_8^+ generated from the reaction of Fe^+ with *n*-butane consists of about 20% $\text{Fe}(\text{C}_2\text{H}_4)_2^+$ and 80% $\text{Fe}(\text{2-butene})^+$.^{19,43,45} However, low ion intensity prevented the isolation of FeC_4H_6^+ from the ligand displacement reaction of $\text{Fe}(\text{C}_2\text{H}_4)_2^+$ with ethyne. It has also been reported that $\text{FeC}_5\text{H}_{10}^+$, produced from the reaction of Fe^+ with *n*-pentane in reaction 9, retains a 1-pentene structure, even though it easily rearranges to bis(alkene) **III** upon activation.⁴³ In accordance with our previous observations,¹⁹ C_2H_4 reacts with $\text{FeC}_5\text{H}_{10}^+$ to produce $\text{Fe}(\text{C}_2\text{H}_4)_2^+$, reaction 10. The reaction of $\text{Fe}(\text{C}_2\text{H}_4)_2^+$ with C_2H_2 results in the formation of FeC_4H_6^+ , which is believed to have an ethene-ethyne structure **II**, reaction 11. To confirm this observation, FeC_4H_6^+ generated in reaction 11 was allowed to react with C_2H_2 , which yielded $\text{Fe}(\text{C}_2\text{H}_2)_2^+$ by ligand displacement, reaction 12. Interestingly, FeC_4H_6^+ made directly from the reaction of $\text{Fe}(\text{1-pentene})^+$ and ethyne yields $\text{Fe}(\text{butadiene})^+$ (**I**), reaction 13, and not $\text{Fe}(\text{C}_2\text{H}_2)(\text{C}_2\text{H}_4)^+$



(II),⁴⁶ $\text{Fe}(\text{butadiene})^+$ is readily distinguished from $\text{Fe}(\text{C}_2\text{H}_2)(\text{C}_2\text{H}_4)^+$ by its reaction with ethyne which, presumably, yields $\text{Fe}(\text{benzene})^+$ and hydrogen instead of proceeding by reaction 12. Even though low ion intensity prevented the IRMPD and SORI of $\text{Fe}(\text{C}_2\text{H}_2)(\text{C}_2\text{H}_4)^+$ from reaction 11, CID of this ion

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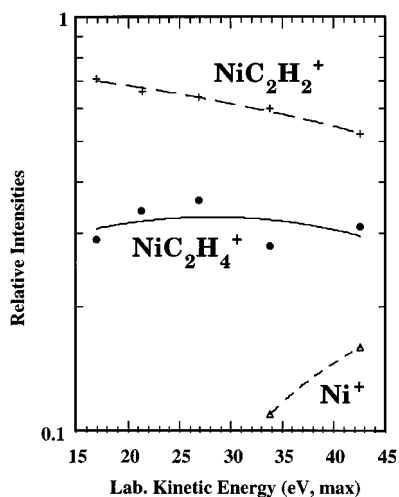
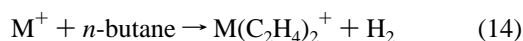


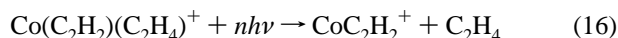
Figure 4. CID of $Ni(C_2H_2)(C_2H_4)^+$ showing that the ion abundance of $NiC_2H_2^+$ is greater than that of $NiC_2H_4^+$.

resulted in the preferential loss of C_2H_4 , indicating $D^\circ(Fe^+ - C_2H_2) > D^\circ(Fe^+ - C_2H_4)$.

$Co(C_2H_2)(C_2H_4)^+$ was prepared by reactions 14 and 15:¹⁹



The $CoC_4H_8^+$ produced in reaction 14 contains about 10–15% $Co(1\text{-butene})^+$.^{19,43} Unfortunately, the $Co(1\text{-butene})^+$ byproduct reacts with C_2H_2 to give a small amount of $Co(\text{butadiene})^+$. IRMPD of $Co(C_2H_2)(C_2H_4)^+$ (**II**) produces equal loss (within experimental error) of C_2H_2 and C_2H_4 (reactions 16 and 17).



Co^+ was also observed, but it most likely is a result of the photodissociation of the product ion, $CoC_2H_4^+$ and, to a small extent, of $Co(\text{butadiene})^+$ (*vide supra*). The contribution of $CoC_2H_2^+$ to the appearance of Co^+ is probably negligible, since this ion was found to be photoinactive.¹⁹ However, the possibility that $CoC_2H_2^+$, produced as a photoproduct with excess internal energy, absorbs infrared photons and dissociates to produce Co^+ cannot be completely ruled out. While the SORI of $Co(C_2H_2)(C_2H_4)^+$ produces $CoC_2H_2^+$ and $CoC_2H_4^+$, exclusively, the CID of this ion produces Co^+ in addition to $CoC_2H_2^+$ and $CoC_2H_4^+$. The ratio of $CoC_2H_2^+$ to $CoC_2H_4^+$ was found to vary between 1.5:1 and 1.8:1 for SORI over the energy range studied, 1–6 eV.

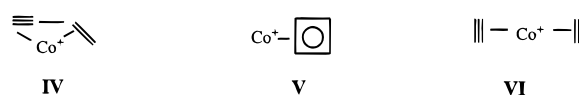
Surprisingly, $Ni(C_2H_2)(C_2H_4)^+$, prepared from reactions 14 and 15, did not undergo IRMPD with up to 3 s irradiation time and 27 W laser power. The SORI and CID of $Ni(C_2H_2)(C_2H_4)^+$ are similar to that of cobalt: exclusive formation of $NiC_2H_4^+$ and $NiC_2H_2^+$ was found in SORI, with additional formation of Ni^+ observed in CID. The amount of $NiC_2H_2^+$ was found to be greater than that of $NiC_2H_4^+$ in SORI and CID (their ratio was found to vary between 1.3:1 and 2.5:1 over the SORI laboratory energy range 1–6 eV). Figure 4 shows the CID profile of $Ni(C_2H_2)(C_2H_4)^+$.

Discussion

M(1,3-butadiene)⁺. Brauman and co-workers have given three criteria for the observation of multiple products in the

IRMPD process: (1) a high rate of infrared photon absorption, (2) a slow dissociation rate associated with the lower energy channel, and (3) a small energy barrier between the high-energy channel and the low-energy channel.⁴⁷ One or all of these criteria can be used to explain the observation of multiple IRMPD products for the undeuterated iron and cobalt ion complexes. The primary reactions of these ions with butadiene clearly indicate that the channels for losses of H_2 , C_2H_4 , and/or C_2H_2 are accessible for Fe^+ and Co^+ . Assuming that observation of the loss of H_2 , HD, etc., indicates that these reaction pathways are at least somewhat exothermic for Fe^+ and Co^+ (Table 5), then these channels must have equal or lower activation barriers than the channel for loss of the deuterated butadiene. Thus, observation of loss of the whole ligand in the IRMPD of $M(\text{butadiene-1,1,4,4-d}_4)^+$ indicates that the rates of formation of $MC_4D_4^+$, $MC_4HD_3^+$, and so forth are sufficiently slow that with an internal energy of as little as 2.7 kcal/mol above the threshold for total ligand loss (i.e., one infrared photon) these channels are not competitive. This isotope effect is also observed in the reactions of Fe^+ and Co^+ with butadiene versus deuterated butadiene, where dehydrogenation is greatly reduced for the latter (Table 5). These results are in accordance with the mechanism in Scheme 1 involving C-H insertion and H transfers, inasmuch as deuterium substitution is known to slow down these processes.¹⁰ Infrared activation has been shown to provide information on the lowest activation energy process.^{1,14,16} This, however, is apparently a case in which infrared activation appears to provide misleading information about the lower energy process. Even though criterion 1 above is generally more appropriate for high power lasers with high pumping rates,^{47,48} in the quasicontinuum and dissociation threshold regimes, low power lasers, like the one used in this experiment, can have sufficient pumping rates to produce multiple products. Therefore, any one or a combination of the three criteria may account for this interesting observation.

Jacobson and co-workers have determined that the structure of $CoC_4H_4^+$, produced in the reaction of Co^+ with butadiene (Table 4), is $Co(1\text{-buten-3-yne})^+$ (**IV**).⁴⁹ It is likely that the iron complex has the analogous structure. Loss of the whole ligand in the SORI and CID of $MC_4H_4^+$ (M = Fe, Co) is in agreement with Jacobson's findings for structure **IV** above, since CID of the cyclobutadiene **V** or bis(acetylene) **VI** structures produce $MC_2H_2^+$ in addition to M^+ .⁴⁹



As mentioned above, a possible mechanism for the loss of H_2 , HD, C_2HD , and C_2HD_3 (Table 5) is given in Scheme 1. Cyclization, producing structure **VII**, with subsequent ring cleavage can yield loss of C_2HD and C_2HD_3 . Loss of H_2 can be rationalized via β -hydrogen transfer from **VII** to form intermediate **VIII**. Other losses given in Table 5 and the



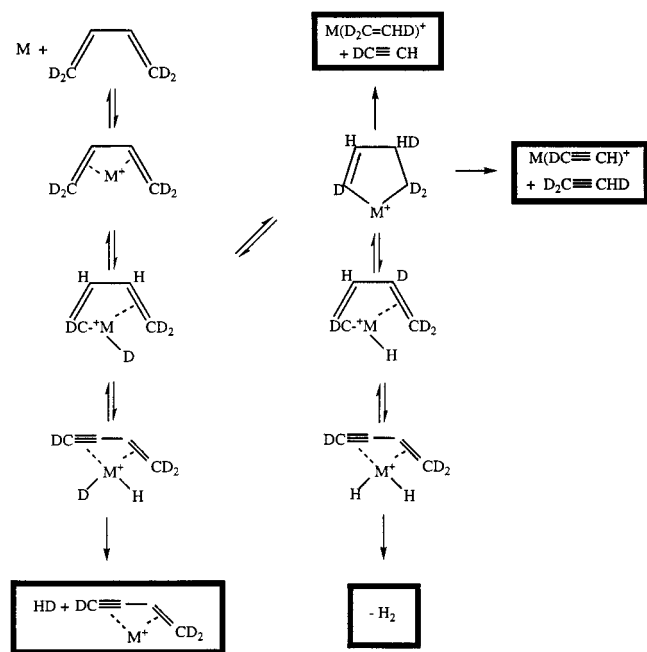
IRMPD products in Table 1 can be explained by this mecha-

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Scheme 1. Mechanism of Reaction for the Decomposition of $M(\text{butadiene-1,1,4,4-d}_4)^+$



nism. Using this mechanism, for example, the structure of m/z 89 is predicted to be $\text{Co}(\text{CHD}=\text{CHD})^+$ and not $\text{Co}(\text{CH}_2=\text{CD}_2)^+$. For cobalt, there were peaks from m/z 85 to 91, except 88. This is in accordance with m/z 88 corresponding to $\text{Co}(\text{C}_2\text{H}_3\text{D})^+$, which is impossible to form since the neutral reagent was $\text{C}_4\text{H}_2\text{D}_4$. In agreement with the absence of FeC_2H_4^+ in the primary reaction of Fe^+ with regular butadiene, $\text{FeC}_2\text{H}_x\text{D}_{4-x}^+$ ($x = 0-2$) were not observed in the reaction of Fe^+ with the deuterated butadiene.

The observation of more products in the IRMPD of MC_4H_6^+ for cobalt than iron and of more extensive scrambling in the reaction of Co^+ when compared to Fe^+ with deuterated butadiene is in agreement with many examples in the gas phase, which suggests that β -hydrogen transfer from an alkene to the metal center is more facile for cobalt compared to iron or nickel.^{21,43,50-53} In addition, insertion of Ni^+ into the C-H bond of butadiene is likely to be less favorable than for Fe^+ and Co^+ , due to the low Ni^+-H bond energy.⁵⁴ This may be responsible in part for the absence of dehydrogenation products during IRMPD and in the reactions of Ni^+ with butadiene.

It is also interesting to note that, while replacing hydrogen with deuterium was observed to increase the photodissociation rate for dimethylchloronium ion⁷ and $M(\text{acetone})_2^+$,⁶ deuteration was observed to decrease the photodissociation rate for $M(1,3\text{-butadiene})^+$. One simple explanation is that, like the presence of the metal ion, deuteration can result in a significant shifting of the absorption band,^{55,56} which may or may not facilitate absorption at 944 cm^{-1} .

$M(\text{C}_2\text{H}_2)(\text{C}_2\text{H}_4)^+$. Lack of dissociation for $\text{Ni}(\text{C}_2\text{H}_2)(\text{C}_2\text{H}_4)^+$ by IRMPD is interesting. Although NiC_2H_2^+ and NiC_2H_4^+ are both photoinactive,¹⁹ $\text{Ni}(\text{C}_2\text{H}_4)_2^+$ is photoactive.¹⁹ Similarly,

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$\text{Al}(\text{acetone})^+$ is photoinactive, but $\text{Al}(\text{acetone})_2^+$ is photoactive.⁶ Therefore, addition of one ligand to the existing photoinactive complex can alter the vibrational distribution and density in the resulting molecule and, as a result, this new molecule can become photoactive at a particular wavelength.

It is also interesting to note that, while IRMPD of $\text{Co}(\text{C}_2\text{H}_2)(\text{C}_2\text{H}_4)^+$ yields equal loss of C_2H_2 and C_2H_4 , SORI and competitive CID of this ion yields more loss of C_2H_4 than C_2H_2 . Therefore, our results suggest that the bond strength of $\text{Co}^+-\text{C}_2\text{H}_2$ is either equal to (by IRMPD) or slightly higher than (by SORI/CID) that of $\text{Co}^+-\text{C}_2\text{H}_4$. However, the results also indicate that these bond strength differences cannot exceed about 2 kcal/mol. The small discrepancy between IRMPD and SORI/CID may arise due to the effect of angular momentum on the outcome of the CID of $\text{Co}(\text{C}_2\text{H}_2)(\text{C}_2\text{H}_4)^+$.⁵⁷ Collisional excitation produces higher rotational states of the ion compared to photon absorption. Because the reduced mass of the $\text{Co}(\text{C}_2\text{H}_2)^+ + \text{C}_2\text{H}_4$ combination is higher than that of the $\text{Co}(\text{C}_2\text{H}_4)^+ + \text{C}_2\text{H}_2$ combination, the former can more readily conserve the angular momentum that gets converted to the orbital angular momentum of the products. Hence, it is likely that IRMPD gives a better representation of the relative bond strengths.

As mentioned above, Bauschlicher and co-workers predicted the bond strength at 0 K of $M^+-\text{C}_2\text{H}_2$ to be 28, 37, and 39 kcal/mol for $M = \text{Fe}, \text{Co},$ and Ni , respectively. For comparison, they predicted the bond strength at 0 K of $M^+-\text{C}_2\text{H}_4$ to be 30, 40, and 41 kcal/mol for $M = \text{Fe}, \text{Co},$ and Ni , respectively.³¹ At 298 K each of these values would increase by about 1 kcal/mol, but their relative order would not change. They attributed these differences to the larger polarizability of C_2H_4 compared to C_2H_2 .^{31b} In contrast, IRMPD, SORI, and competitive CID indicate $D^\circ(\text{Co}^+-\text{C}_2\text{H}_2) \geq D^\circ(\text{Co}^+-\text{C}_2\text{H}_4)$, SORI and competitive CID indicate $D^\circ(\text{Ni}^+-\text{C}_2\text{H}_2) > D^\circ(\text{Ni}^+-\text{C}_2\text{H}_4)$, and competitive CID indicates $D^\circ(\text{Fe}^+-\text{C}_2\text{H}_2) > D^\circ(\text{Fe}^+-\text{C}_2\text{H}_4)$. However, both the calculations and the experiments indicate that the bond energies for C_2H_2 and C_2H_4 are within 3 kcal/mol of each other.

Thus, we assign $D^\circ(\text{Co}^+-\text{C}_2\text{H}_2) = 43 \pm 2$ kcal/mol on the basis of $D^\circ(\text{Co}^+-\text{C}_2\text{H}_2) \sim D^\circ(\text{Co}^+-\text{C}_2\text{H}_4) = 42.9 \pm 1.6$ kcal/mol^{30a} and $D^\circ(\text{Fe}^+-\text{C}_2\text{H}_2) = 36 \pm 2$ on the basis of $D^\circ(\text{Fe}^+-\text{C}_2\text{H}_2) > D^\circ(\text{Fe}^+-\text{C}_2\text{H}_4) = 34.7 \pm 1.4$ kcal/mol.³⁴ An estimate for $D^\circ(\text{Ni}^+-\text{C}_2\text{H}_2) = 45 \pm 2$ kcal/mol and $D^\circ(\text{Ni}^+-\text{C}_2\text{H}_4) = 44 \pm 2$ kcal/mol is derived from the theoretical calculations indicating that $D^\circ(\text{Ni}^+-\text{C}_2\text{H}_2)$ is about 2 kcal/mol higher than $D^\circ(\text{Co}^+-\text{C}_2\text{H}_2)$, and $D^\circ(\text{Ni}^+-\text{C}_2\text{H}_4)$ is about 1 kcal/mol higher than $D^\circ(\text{Co}^+-\text{C}_2\text{H}_4)$.^{31a}

Our assigned value of $D^\circ(\text{Fe}^+-\text{C}_2\text{H}_2) = 36 \pm 2$ kcal/mol is in good agreement with an earlier value of 32 ± 6 kcal/mol based on ion-molecule bracketing experiments,^{30d} while our value of $D^\circ(\text{Co}^+-\text{C}_2\text{H}_2) = 43 \pm 2$ kcal/mol is about 3 kcal/mol higher than the earlier reported value of 39.7 kcal/mol.^{30a} This difference is easily explained, however. Both of the cobalt values are anchored to the ion beam measurement of $D^\circ(\text{Co}^+-\text{C}_2\text{H}_4) = 42.9$ kcal/mol, but while our experiments gave $D^\circ(\text{Co}^+-\text{C}_2\text{H}_2) \sim D^\circ(\text{Co}^+-\text{C}_2\text{H}_4)$, the latter value was estimated from the theoretical results above, indicating that $D^\circ(\text{Co}^+-\text{C}_2\text{H}_2) = D^\circ(\text{Co}^+-\text{C}_2\text{H}_4) - 3$ kcal/mol.

Finally, observation of $M(\text{C}_2\text{H}_4)^+$ and/or $M(\text{C}_2\text{H}_2)^+$ in the

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reactions of M^+ with butadiene implies $D^\circ(M^+-C_2H_4)$ and/or $D^\circ(M^+-C_2H_2) \geq 40.3$ kcal/mol. This is the amount of energy required to convert butadiene into C_2H_4 and C_2H_2 .^{58,59} While these limits are in accordance with the assigned bond energies for Co^+ , the observation of $Fe(C_2H_2)^+$ is apparently from an endothermic reaction. It may be explained by the presence of a small amount (~8%) of excited state iron which was not quenched by the cooling procedure.⁴¹ In contrast, the formation of $Ni(C_2H_2)^+$ and $Ni(C_2H_4)^+$ from butadiene is certainly exothermic but is not observed. Thus, an activation barrier in

the reaction pathway prevents a dissociative reaction from occurring with Ni^+ .

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