1118 *J. Am. Chem. Soc.* **1996,** *118,* 1118−1125

Infrared Multiphoton Dissociation of Transition Metal Containing Ions: $MC_nH_{2n}^+$ (M = Fe, Co, Ni; $n = 2-5$)

Paul I. Surya, Lisa M. Roth, Don Rufus A. Ranatunga, and Ben S. Freiser*

Contribution from the H. C. Brown Laboratory of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393

Received November 16, 1994[⊗]

Abstract: The infrared multiphoton dissociation (IRMPD) processes of groups 8−10 (Fe, Co, Ni) transition metal ion complexes containing acetylene and alkenes were investigated. Of the 30 ions studied, all but four were found to be photoactive at 944 cm^{-1}, the wavelength of the CO_2 infrared laser employed. Most of the ions were observed to yield one photodissociation product, as is typical for IRMPD. Ironacyclopentane, nickelacyclopentane, $Co(isobutene)^+$, and $Ni(isobutene)^+$, however, were observed to give multiple products. This observation is a result of kinetic and thermodynamic factors, and it gives information about the potential energy surface of the dissociating ion. More specifically, activation barrier heights leading to the product ions can be probed. Sustained off-resonance irradiation, an experiment designed to mimic infrared activation, was also performed on these ions, yielding results in good agreement with the infrared results.

Introduction

Infrared multiphoton dissociation (IRMPD) represents one in an arsenal of techniques to probe gas-phase ionic structures. In the past 15 years, it has been employed to obtain fundamental information on unimolecular and bimolecular reaction dynamics,[1,2] vibrational relaxation,[3] photoinduced reactions,[4,5] vibrationally induced electron detachment,[6] fluence saturation phenomena,[7] wavelength dependence in the quasi-continuum,[8] gas-phase ion spectra of organic and organometallic species,[9−12] isotopic and isomeric selectivity,[13−15] the McLafferty rearrangement,[16] and gas-phase S_N2 reactions.[17] However, while this method has been applied successfully to many organic structures,[5,18−24] surprisingly few papers have appeared that deal with metal-containing ions.[4,9,10,13,25] This paper extends the use of the infrared multiphoton experiment to study the photodissociation characteristics of groups 8−10 (Fe, Co, Ni) transition metal ion complexes containing acetylene and alkenes.

In IRMPD, energy is added to the ion in small increments in a stepwise fashion until an activation barrier for dissociation is surpassed, at which point dissociation occurs. The observation of more than one product under IRMPD for ions is not common.[4,13,26,27] While such an observation may indicate the presence of a mixture of isomers, in the event that it arises from a single isomer, it suggests the presence of common activation barriers. In this work, multiple products are observed in four cases. This paper addresses possible explanations for such observations.

Jacobson and co-workers have developed an alternative technique that mimics infrared activation which they have termed sustained off-resonance irradiation (SORI).[28] By choosing the appropriate time and frequency of excitation, ions undergo collisions during multiple acceleration and deceleration cycles and, as a result, the internal energies of the ions are increased by increments until there is sufficient energy to cause dissociation in analogy to infrared activation. This paper provides further evidence that the SORI and IRMPD techniques yield similar product distributions.

Experimental Section

Experiments were performed on a Nicolet FTMS-2000 Fourier transform ion cyclotron resonance (FTICR) mass spectrometer.[29,30] This instrument features a dual-cell arrangement that permits ion transfer

---

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

(1) Bomse, D. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 3292.

(2) Bomse, D. S.; Berman, D. W.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 3968.

(3) Jasinski, J. M.; Brauman, J. I. *J. Chem. Phys.* **1980**, *73*, 6191.

(4) Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1993**, *115*, 737.

(5) Bomse, D. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 3967.

(6) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *J. Chem. Phys.* **1979**, *71*, 1030.

(7) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *Chem. Phys. Lett.* **1980**, *71*, 400.

(8) Coggiola, M. J.; Cosby, P. C.; Peterson, J. R. *J. Chem. Phys.* **1980**, *72*, 6507.

(9) Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 2057.

(10) Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 2066.

(11) Woodin, R. L.; Bomse, D. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1979**, *63*, 630.

(12) Shin, S. K.; Beauchamp, J. L. *J. Mol. Struct.* **1991**, *249*, 1.

(13) Surjasasmita, P. I.; Freiser, B. S. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 135.

(14) Bomse, D. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1981**, *77*, 25.

(15) Wight, C. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6499.

(16) Osterheld, T. H.; Brauman, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 2014.

(17) Wilbur, J. L.; Brauman, J. I. *J. Am. Chem. Soc.* **1991**, *113*, 9699.

(18) Thorne, L. R.; Beauchamp, J. L. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. 3, Chapter 18.

(19) Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5503.

(20) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1982**, *104*, 658.

(21) Jasinski, J. M.; Rosenfeld, R. N.; Meyer, F. K.; Brauman, J. I. *J. Am. Chem. Soc.* **1982**, *104*, 652.

(22) Baykut, G.; Watson, C. H.; Weller, R. R.; Eyler, J. R. *J. Am. Chem. Soc.***1985**, *107*, 8036.

(23) Watson, C. H.; Baykut, G.; Battiste, M. A.; Eyler, J. R. *Anal. Chim. Acta* **1985**, *178*, 125.

(24) Bensimon, M.; Rapin, J.; Gaumann, T. *Int. J. Mass Spectrom. Ion Processes* **1986**, *72*, 125.

(25) Hanratty, M. A.; Paulsen, C. M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 5074.

(26) Johnson, C. E.; Brauman, J. I. In *Techniques for the Study of Ion Molecule Reactions*; Farrar, J. M., Sauders, W. H., Jr., Eds., John Wiley and Sons: New York, 1988; Chapter 10.

(27) Moini, M.; Eyler, J. R. *Int. J. Mass Spectrom. Ion Processes* **1987**, *76*, 47.

(28) Gauthier, J. W.; Trautman, T. R.; Jacobson, D. B. *Anal. Chim. Acta* **1991**, *246*, 211.

(29) Cody, R. B.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *41*, 199.

0002-7863/96/1518-1118$12.00/0

between the source cell and the analyzer cell, and which is situated in the bore of a 3.0 T superconducting magnet. The metal ions were generated by laser desorption using the fundamental output of a Quanta Ray Nd:YAG laser (1.06 μm) focused onto the metal target.[31] After their formation, the metal ions were cooled with argon gas (at ~1 × 10^{-6} Torr) for 2 s in order to remove the excess electronic and kinetic energy.[32,33]

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 setup of the infrared laser coupled to the FTMS-2000 instrument in our laboratory is similar to that described elsewhere.[19,21,22] The beam diameter of the CO_2 laser (fwhm) at a distance between the laser aperture and the cell of 318 cm was measured to be 7.1 mm. Irradiances were typically on the order of 4.5−24 W (corrected for reflective losses) for 0.1−10 s trapping time. A Uniblitz mechanical shutter Model VS25S2W0 was used to gate the infrared laser. An uncalibrated Coherent Model 201 power meter was used to monitor the nominal power of the CO_2 laser. Unless otherwise noted, the percentage of IRMPD fragmentation reported has a ±10% uncertainty.

Since the instrument has a dual cell, there are two ways to isolate a parent ion before it is irradiated with the infrared laser: one involves parent ion transfer and the other does not. In the first method, the metal ions were allowed to react with the reagent in the analyzer side and then the selected product ions were transferred to the source side where they were irradiated with the infrared laser in the absence of argon background pressure. In the second method, the metal ions were trapped directly in the source side where, after a cooling period, they were allowed to react with the reagent and the resulting product ions were irradiated in the presence of a background of argon gas (usually at ~1 × 10^{-6} Torr). Even though the effect of the argon gas was usually to decrease the photodissociation yield,[19] these two methods yielded the same product and, in the case when two or more products appeared, both methods gave the same product ratios within 5%. Whenever photodissociation yields were qualitatively compared, every attempt was made to prepare the ions by the same method under identical conditions.

Collision-induced dissociation (CID) was performed using argon as the collision gas at a pressure of ~(1−2) × 10^{-6} Torr.[34] The collision energy of the ions can be varied typically between 0 and 150 eV (reported as laboratory collision energy). For the SORI experiments,[28] argon ((1−2) × 10^{-6} Torr) was also used as the collision gas. Either the amplitude of the off-resonance electric field (the excitation voltage) or the frequency of excitation was varied to obtain the optimum SORI conditions. 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 and ratio of the products at some point become essentially constant. Attempts at going lower in energy resulted in a poor signal. Unless otherwise noted, the percentage of CID and SORI fragmentation reported has a 10% uncertainty.

Results and Discussion

$MC_2H_2^+$, $MC_2H_4^+$, and $MC_3H_6^+$. $MC_2H_2^+$ ions were generated by displacement of C_2H_4 from $MC_2H_4^+$ by C_2H_2 (reactions 1 and 2). $MC_2H_4^+$ and $MC_3H_6^+$ were prepared from the reactions of M^+ with propane (reactions 3 and 4).[34] While $MC_2H_2^+$ (M = Fe, Co, Ni) and $NiC_2H_4^+$ were photoinactive at 944 cm^{-1} (5 s, 22 W), the remainder of the ions underwent photodissociation by loss of the whole ligand (reactions 5 and 6). In addition, SORI on these ions also produced the bare metal ions, exclusively.

$$M^+ + n\text{-pentane} \rightarrow MC_2H_4^+ + C_3H_8 \qquad (1)$$

$$MC_2H_4^+ + C_2H_2 \rightarrow MC_2H_2^+ + C_2H_4 \qquad (2)$$

$$M^+ + \text{propane} \rightarrow MC_2H_4^+ + CH_4 \qquad (3)$$

$$\rightarrow MC_3H_6^+ + H_2 \qquad (4)$$

$$(M = Fe, Co, Ni)$$

$$MC_2H_4^+ + nh\nu \rightarrow M^+ + C_2H_4 \qquad (5)$$

$$(M = Fe, Co)$$

$$MC_3H_6^+ + nh\nu \rightarrow M^+ + C_3H_6 \qquad (6)$$

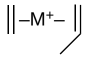
$$(M = Fe, Co, Ni)$$

The relative photodissociation cross sections based on the extent of photodissociation follow the order

$$FeC_3H_6^+ > CoC_3H_6^+ > NiC_3H_6^+ > FeC_2H_4^+ > CoC_2H_4^+ > NiC_2H_4^+$$

CID of $MC_2H_2^+$ yielded the bare metal ions. CID of $MC_2H_4^+$ and $MC_3H_6^+$ have been reported; they also yielded the bare metal ions, exclusively.[34]

$MC_4H_8^+$: (A) $M(C_2H_4)_2^+$. $Fe(C_2H_4)_2^+$ and $Co(C_2H_4)_2^+$ were generated by displacement of propene from $MC_5H_{10}^+$ by ethene [reactions 7 and 8; the reaction between M^+ with *n*-pentane produces other products in addition to $MC_5H_{10}^+$, including $MC_2H_4^+$ (reaction 1)].[35] Jacobson and Freiser have shown that the reaction of Co^+ with *n*-pentane generates $CoC_5H_{10}^+$ in the form of bis(alkene) **1**.[34] Iron, on the other hand, reacts with *n*-pentane to generate mainly Fe(1-pentene)$^+$. However, upon activation this ion easily rearranges to bis(alkene) **1**.[34] $Ni(C_2H_4)_2^+$ was simply generated by the well characterized reaction between Ni^+ and *n*-butane (reaction 9).[36]



1

$$M^+ + n\text{-pentane} \rightarrow MC_5H_{10}^+ + H_2 \qquad (7)$$

$$MC_5H_{10}^+ + C_2H_4 \rightarrow M(C_2H_4)_2^+ + C_3H_6 \qquad (8)$$

$$(M = Fe, Co)$$

$$Ni^+ + n\text{-butane} \rightarrow Ni(C_2H_4)_2^+ + H_2 \qquad (9)$$

Infrared activation of $M(C_2H_4)_2^+$ yields loss of C_2H_4, exclusively (reaction 10). That loss of H_2 was not observed for the IRMPD of these ions indicates that no ligand coupling occurs between the two ethenes even upon activation, which confirms an earlier suggestion by Beauchamp and co-workers that the activation barriers for this coupling are significant in

---

[30] Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.

[31] Cody, R. B.; Burnier, R. C.; Reents Jr., W. D.; Carlin, T. J.; McCrery, D. A.; Lengel, R. K.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 37.

[32] Armentrout, P. B. In *Gas Phase Inorganic Chemistry*; Russell, D. H., Ed.; Plenum Press: New York, 1989.

[33] Freiser, B. S. *Talanta* **1985**, *32*, 697.

[34] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.

[35] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.

[36] Halle, L. F.; Houriet, R.; Kappes, M. M.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6293.

the case of $Co(C_2H_4)_2^+$.[37] CID of $M(C_2H_4)_2^+$ produced loss of C_2H_4 at low energy, together with $2C_2H_4$ at high energy.

$$M(C_2H_4)_2^+ + nh\nu \rightarrow MC_2H_4^+ + C_2H_4 \qquad (10)$$

$$(M = Fe, Co, Ni)$$

(B) $MC_4H_8^+$ (C_4H_8 = 1-Butene, *cis*-2-Butene, and *trans*-2-Butene). These $MC_4H_8^+$ ions were generated by displacement of CO from MCO^+ by C_4H_8 (reactions 11 and 12).[13,36,38] The infrared activation and SORI of $MC_4H_8^+$ yield loss of H_2, exclusively (reaction 13). It has been previously shown that $MC_4H_6^+$ in these cases have 1,3-butadiene structures.[39,40] As reported earlier,[38,41] CID of $MC_4H_8^+$ also yields loss of H_2 at low energy, together with loss of C_4H_8 at high energy.

$$M^+ + \text{acetone} \rightarrow MCO^+ + C_2H_6 \qquad (11)$$

$$MCO^+ + C_4H_8 \rightarrow MC_4H_8^+ + CO \qquad (12)$$

$$MC_4H_8^+ \xrightarrow{nh\nu/\text{SORI}} MC_4H_6^+ + H_2 \qquad (13)$$

$$(M = Fe, Co, Ni; C_4H_8 = \text{1-butene}, \textit{cis}\text{-2-butene}, \textit{trans}\text{-2-butene})$$

The IRMPD efficiency follows the order

$$\text{Co(1-butene)}^+ \approx \text{Co}(\textit{cis}\text{-2-butene})^+ \approx \text{Co}(\textit{trans}\text{-2-butene})^+ > \text{Fe(1-butene)}^+ \approx \text{Fe}(\textit{cis}\text{-2-butene})^+ \approx \text{Fe}(\textit{trans}\text{-2-butene})^+ > \text{Ni(1-butene)}^+ \approx \text{Ni}(\textit{cis}\text{-2-butene})^+ \approx \text{Ni}(\textit{trans}\text{-2-butene})^+$$

Unfortunately, the similarity in IRMPD, SORI, and CID cross sections for these $MC_4H_8^+$ isomers makes them difficult to distinguish from each other using these methods alone.

Finally, it is interesting to note that while the infrared activation of Co(1-butene)$^+$ gives identical products to that of Co(2-butene)$^+$, infrared activation of Co(1-pentene)$^+$ yields C_2H_4 loss while that of Co(2-pentene)$^+$ produces loss of CH_4.[25] The difference between cobalt complexes with pentenes and butenes lies in the initial metal−ligand interaction: for pentene, C−C insertion at the allylic position prevails over a C−H insertion and is followed by β-hydrogen transfer;[25] for butene, C−H insertion takes preference over C−C insertion, and this is followed by β-hydrogen transfer.[34,38] This results in generating a common intermediate for both 1- and 2-butene. C-H insertion also dominates the M^+ chemistry of butenes.[39,40,42]

(C) $MC_4H_8^+$ from the Reaction of M^+ with *n*-Heptane. The reactions of M^+ with linear alkanes larger than *n*-butane produce $MC_4H_8^+$ as one of the reaction products which, most likely, has a M(1-butene)$^+$ structure.[34] $MC_4H_8^+$ generated from the reaction of M^+ with *n*-heptane (reaction 14) undergoes IRMPD to produce, exclusively, $MC_4H_6^+$ by H_2 loss (reaction 15, Tables 1−3). These results are consistent with the reference butene ions above, although the specific isomer cannot be distinguished from this experiment alone.

Table 1. IRMPD on $CoC_4H_8^+$ Product Ions Generated from the Reactions of Co^+ with Organic

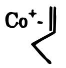
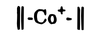
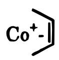
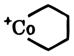
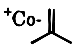
Organic compound	$CoC_4H_8^+$ isomer		Product(s), % $CoC_4H_6^+$	$CoC_2H_4^+$	Co^+
n-heptane			100		
n-butane		90±5%		100	
		10±5%	100		
cyclo-pentanone			100		
isobutane			67	15	18

Table 2. IRMPD on $FeC_4H_8^+$ Product Ions Generated from the Reactions of Fe^+ with Organic

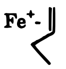
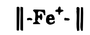
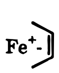
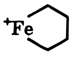
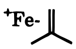
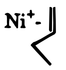
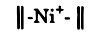
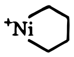
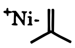
Organic compound	$FeC_4H_8^+$ isomer		Product(s), % $FeC_4H_6^+$	$FeC_2H_4^+$	Fe^+
n-heptane			100		
n-butane		20±5%		100	
		80±5%	100		
cyclo-pentanone			< 53	> 47	
isobutane					100

Table 3. IRMPD on $NiC_4H_8^+$ Product Ions Generated from the Reactions of Ni^+ with Organic

Organic compound	$NiC_4H_8^+$ isomer	Product(s), % $NiC_4H_6^+$	$NiC_2H_4^+$
n-heptane		100	
n-butane			100
cyclo-pentanone		< 62	> 38
isobutane		92	8

$$M^+ + n\text{-heptane} \rightarrow MC_4H_8^+ + C_3H_8 \qquad (14)$$

$$MC_4H_8^+ + nh\nu \rightarrow MC_4H_6^+ + H_2 \qquad (15)$$

$$(M = Fe, Co, Ni)$$

(D) $MC_4H_8^+$ from the Reaction of M^+ with *n*-Butane. Ion−molecule reactions between M^+ and *n*-butane have been studied extensively.[34,43−46] One of the reaction pathways

---

[37] Halle, L. F.; Crowe, W. E.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1984**, *3*, 1694.

[38] Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912.

[39] Hettich, R. L.; Freiser, B. S. *Organometallics* **1989**, *8*, 2447.

[40] Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624.

[41] Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 4307.

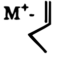
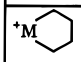
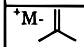
[42] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484.

[43] Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; van Koppen, P.; Bowers, M. T. *J. Am. Chem. Soc.* **1988**, *110*, 1.

[44] Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963.

[45] Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784.

Table 4. IRMPD, CID, and UV–Vis Photodissociation of $MC_4H_8^+$

Structure	IRMPD			CID			UV/VIS PDS[b]
	neutral(s) lost						
	Fe	Co	Ni	Fe	Co	Ni	Ni
	H_2	H_2	H_2	H_2[a] C_4H_8	H_2[a] C_4H_8	H_2[a] C_4H_8	H_2 CH_3 C_2H_4 C_4H_8
‖-M^+- ‖	C_2H_4	C_2H_4	C_2H_4	C_2H_4[a] 2 C_2H_4	C_2H_4[a] 2 C_2H_4	C_2H_4[a] 2 C_2H_4	C_2H_4 2 C_2H_4
	H_2 C_2H_4	H_2	H_2 C_2H_4	H_2[a] C_2H_4 C_4H_8	H_2 C_2H_4 C_4H_8	H_2[a] C_2H_4 C_4H_8	H_2 C_2H_4 C_4H_8
	C_4H_8	H_2 C_2H_4 C_4H_8	H_2 C_2H_4	C_4H_8[a]	H_2 C_2H_4 C_4H_8	H_2 C_2H_4	CH_4 C_4H_8

[a] Reference 34. [b] Reference 64. No data is available for Fe^+ or Co^+ for UV/VIS photodissociation.

between M^+ and *n*-butane is dehydrogenation (reaction 16, Tables 1–3). For M = Co, exhaustive infrared photodissociation,[47] where the parent ion is photodissociated to completion or near completion, yielded two products, namely $CoC_2H_4^+$ (90%) and $CoC_4H_6^+$ (10%). Since results from the reference ions above showed that IRMPD of $Co(C_2H_4)_2^+$ produces loss of C_2H_4 and IRMPD of Co(1- or 2-butene)$^+$ produces loss of H_2, a logical conclusion is that the observation of two photoproducts in the IRMPD of $CoC_4H_8^+$ from *n*-butane indicates a mixture of 90% $Co(C_2H_4)_2^+$ and 10% Co(butene)$^+$ (5% error). In addition, an exhaustive SORI experiment gave 84 ± 5% and 16 ± 5%, respectively. In this instance, it was necessary to perform exhaustive infrared and SORI dissociation experiments to obtain the correct ratio of the isomers present, since these isomers have different infrared and SORI cross sections.[47]

$$M^+ + n\text{-butane} \rightarrow MC_4H_8^+ + H_2 \qquad (16)$$

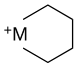
$$(M = Fe, Co, Ni)$$

For iron, exhaustive infrared photodissociation shows that $FeC_4H_8^+$, produced from *n*-butane, consists of 20 ± 5% $Fe(C_2H_4)_2^+$ and 80 ± 5% Fe(butene)$^+$. In addition, exhaustive SORI gives 16 ± 5% and 84 ± 5%, respectively.[47] As mentioned above, IRMPD of $NiC_4H_8^+$, produced from *n*-butane, yields loss of C_2H_4, exclusively, indicating that no Ni(butene)$^+$ is present. The cobalt, iron, and nickel results are in excellent agreement with previous studies using other methods.[34,36,38,43]

(E) $MC_4H_8^+$ from the Reaction of M^+ with Cyclopentanone. M^+ reacts with cyclopentanone to yield several products including $MC_4H_8^+$, which is believed to have a metallacyclopentane structure **2**, and $MC_4H_6^+$ which is believed to be M(1,3-butadiene)$^+$ (reactions 17 and 18).[34,36,48] For M = Co, even though the product ion abundance of $CoC_4H_8^+$ from reaction 17 is low (less than 10%) and, therefore, was not investigated in the earlier study,[34] due to SWIFT technology,[49,50] the isolation and subsequent structural characterization of this ion could be performed. $CoC_4H_8^+$, produced in reaction 17, underwent IRMPD exclusively by loss of H_2 to produce, presumably, Co(1,3-butadiene)$^+$ (Tables 1 and 4). In contrast, CID of $CoC_4H_8^+$ at 33 eV laboratory energy produces loss of H_2, C_2H_4, and C_4H_8 in the ratio of 63/20/17. In addition, SORI of this ion at 2.5 eV laboratory energy produces loss of H_2 and C_2H_4, 90/10. $FeC_4H_8^+$ and $NiC_4H_8^+$, on the other hand, underwent IRMPD to produce loss of H_2 and C_2H_4 in the ratio of 53/47 for iron and 62/38 for nickel. Losses of H_2 and C_2H_4 were also observed for SORI in the ratio of 48/52 for iron and 53/47 for nickel. The IRMPD and SORI results of $MC_4H_8^+$ (M = Fe, Co, and Ni), formed in reaction 17, are shown in Table 5.

Table 5. IRMPD vs SORI for $MC_4H_8^+$ (M = Fe, Co, Ni) from the Reaction of M^+ with Cyclopentanone

			SORI		
	IRMPD: neutral(s) lost, %		energy, eV (laboratory)	neutral(s) lost, %	
M	H_2	C_2H_4		H_2	C_2H_4
Fe	53	47	1.6	48	52
Co	100	0	2.5	90	10
Ni	62	38	2.6	53	47



2

$$M^+ + \text{cyclopentanone} \rightarrow MC_4H_8^+ + CO \qquad (17)$$

$$\rightarrow MC_4H_6^+ + CO + H_2 \qquad (18)$$

$$(M = Fe, Co, Ni)$$

While ligand displacement experiments clearly indicate that a bis(ethene)–metal ion structure is not present for iron and nickel,[34,36,48] for cobalt such evidence comes from the infrared activation: loss of C_2H_4 would have been observed if $CoC_4H_8^+$ contained a bis(ethene) structure (*vide supra*). However, it is possible that loss of H_2 in the IRMPD of $CoC_4H_8^+$ also comes, in part, from a butene–cobalt ion structure, since these two ions yield the same photoproduct. That is to say, the absence of a Co(butene)$^+$ isomer cannot be ruled out on the basis of the present data.

Beauchamp and co-workers earlier proposed a simplified reaction coordinate diagram for the decomposition of the cobaltacyclopentane ion.[37] From that diagram, it appears that a significant energy barrier exists between bis(ethene)cobalt ion **3** (M = Co) and cobaltacyclopentane **2** (M = Co) and that this barrier is higher than those between cobaltacyclopentane ion **2** (M = Co) and dehydrogenation to 1,3-butadiene–cobalt ion,

‖–M^+– ‖

3

---

(46) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818.

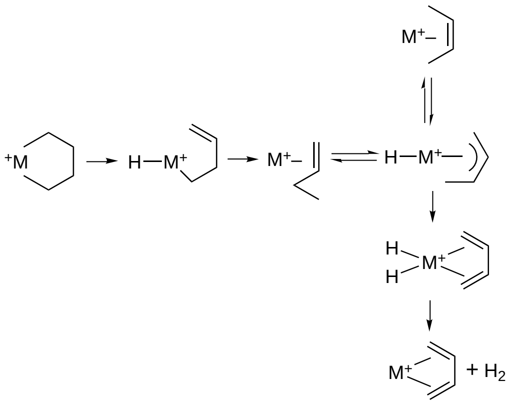
(47) Surjasasmita, I. B. Ph.D. Thesis, Purdue University, West Lafayette, IN, 1993.

(48) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736.

(49) Marshall, A. G.; Wang, T.-C. L.; Ricca, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 7893.

(50) Wang, T.-C. L.; Ricca, T. L.; Marshall, A. G. *Anal. Chem.* **1986**, *58*, 2935.

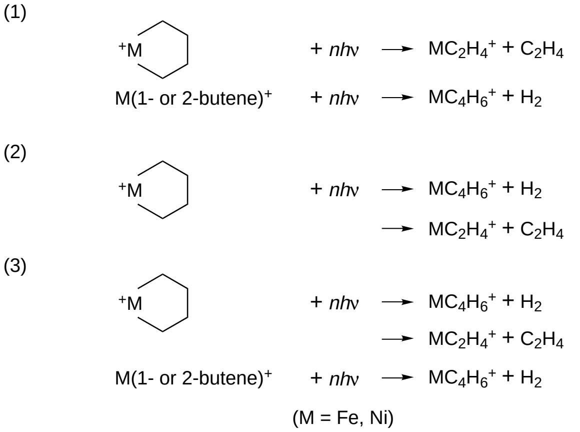
Scheme 1. Mechanism for the Formation of $MC_4H_6^+$ from Metallacyclopentane[a]



[a] Adapted from ref 51.

such that the infrared activation favors dehydrogenation, exclusively, over loss of ethene. Finally, loss of hydrogen in the infrared activation of cobaltacyclopentane ion is in agreement with many examples in the gas phase which show dehydrogenation is a facile process for both cobalt−alkene and/or cobaltacycloalkane compared to their iron and nickel counterparts.[34,37,39,45,46,51]

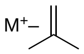
The observation of two photoproducts for irona- and nickelacyclopentane is interesting. As mentioned earlier, such an observation can arise from a mixture of two isomers. In fact, Larsen[38] and Peake[41] have suggested that in addition to ironacyclopentane ion, reaction 17 also produces Fe(1- or 2-butene)$^+$. Since the presence of bis(ethene)M^+ has been ruled out,[34,36,48] we can eliminate it as a possible explanation for the IRMPD results of $MC_4H_8^+$ from reaction 17. Thus, we are left with three possibilities:



Examination of the mechanism of formation of $MC_4H_8^+$ [37] and $MC_4H_6^+$ (Scheme 1) from cyclopentanone and the thermochemistry of reactions 17 and 18[52] suggests that the formation of $MC_4H_6^+$, reaction 18, is likely to be a result of the exothermicity of the formation of $MC_4H_8^+$, reaction 17, and not due to a different route of the initial metal−cyclopentanone interaction. Apparently, however, this exothermicity is not enough to overcome the barrier for the formation of a bis(ethene)metal complex **3**. Thus, the activation energy for the conversion of metallacyclopentane ion **2** to form bis(ethene) **3** is higher than that to form a butadiene complex. Consequently, the possibility that IRMPD favors a higher channel (through symmetric ring cleavage[34] to produce $MC_2H_4^+$) to a lower channel (to produce butadiene) can be ruled out. The second possibility may also be ruled out since, as mentioned above, it has been suggested that reaction 18 also involves the 1- or 2-butene−metal complex.[38,41] Thus, in accordance with the earlier studies, the third possibility is the most likely to account for the observed IRMPD behavior. As a result, the amount of $MC_4H_6^+$ observed in the photodissociation is partly due to the contribution of M(1- or 2-butene)$^+$. Accordingly, it is more accurate to state that metallacyclopentane ion **2** alone undergoes IRMPD to lose H_2 and C_2H_4 with the ratio of $<53/>47$ for iron and $<62/>38$ for nickel rather than simply 53/47 and 62/38, respectively.

Brauman gave three criteria for the observation of multiple products from a single ion structure: (1) the rate of infrared photon absorption is sufficiently high, (2) the dissociation rate of the lower energy channel is low, and (3) the energy barrier differences between the higher channel and the lower channel are sufficiently small.[53] Brauman estimated that for an ion with a typical cross section σ_d of 10^{-19} cm^2, using a pulsed laser with a typical photon flux $\Phi = 10^{26}$ photons cm^{-2} s^{-1} yields a typical rate constant for infrared pumping of 10^7 s^{-1}.[53] For cw lasers, on the other hand, a typical pumping rate constant is only $2-100$ s^{-1}.[18] Therefore, while criterion 1 could conceivably be important with high-power lasers,[54] criteria 2 and 3 are more appropriate with low-power cw lasers. For example, Bomse and Beauchamp attributed the observation of three products upon low-power cw infrared activation of proton bound *n*-propyl alcohol dimer, $(C_3H_7OH)_2H^+$, to a common transition state shared by the products.[1] Similarly, the observation of both $MC_2H_4^+$ and $MC_4H_6^+$ in the IRMPD of $MC_4H_8^+$ (M = Fe, Ni), produced from cyclopentanone, suggests that these two channels either share a common activation barrier or have nearly the same barriers. In addition, the rate of dissociation for ethene formation is slightly higher than that of butadiene formation. In agreement with the above, the formation of $MC_2H_4^+$ requires fewer steps and has a deeper well and, therefore, a higher vibrational state density compared to the formation of $MC_4H_6^+$.

(F) $MC_4H_8^+$ from the Reaction of M^+ with Isobutane. The last set of isomers studied in the series of $MC_4H_8^+$ is M(isobutene)$^+$ **4**, generated from the reaction of M^+ with isobutane



4

(reaction 19). The IRMPD of Fe(isobutene)$^+$ yielded loss of the whole ligand. Infrared activation of Co(isobutene)$^+$, however, was observed to yield three photoproducts by dehydrogenation, loss of ethene, and loss of C_4H_8 (reactions 20−22, Table 1). Care has been taken to ensure the authenticity of this surprising finding. In this instance, the parent ion has been generated with and without ion transfer. Also, to rule out the possibility of irradiating a mixture of isomers to start with, Co(isobutene)$^+$ was also generated by a ligand displacement reaction (reactions 23 and 24) in the analyzer side and subsequently transferred to the source side prior to irradiation under nearly collisionless conditions. Indeed, the above three experiments give identical results within experimental error. Loss of H_2 and C_2H_4 was observed for the infrared activation

---

(51) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492.

(52) Reactions 17 and 18 are exothermic by 12.6 and 1.5 kcal/mol, respectively. These numbers are obtained by using the value of $\Delta H_f°_{298}$(•$CH_2CH_2CH_2CH_2$•) as 60.9 kcal/mol and other thermochemical data as listed on Table 8. $\Delta H_f°_{298}$ (•$CH_2CH_2CH_2CH_2$•), in turn, is calculated by using the value of $\Delta H_f°_{298}$ (*n*-C_4H_9) as 15.29 kcal/mol (ref 69).

(53) Moylan, C. R.; Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1985**, *107*, 1394.

(54) Farneth, W. E.; Thomsen, M. W.; Berg, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 6468.

Table 6. SORI of M(isobutene)$^+$ (M = Fe, Co, Ni) from the Reaction of M$^+$ with Isobutane

		neutral(s) lost, %		
energy, eV (laboratory)	M	H_2	C_2H_4	C_4H_8
at all energies (1.0-6.5 eV)	Fe			100
2.5	Co	55	6	39
5.1	Ni	77	6	17

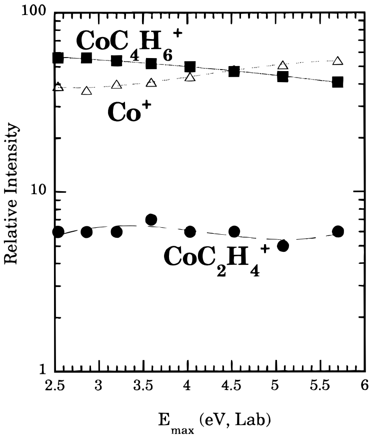


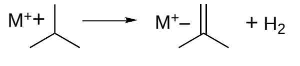
Figure 1. SORI of Co(isobutene)$^+$ from the reaction of Co$^+$ with isobutane.

Table 7. Product Distributions for the Reactions of M$^+$ with Isobutene

	neutral(s) lost, %			
M	no neutal lost	H_2	CH_4	C_2H_4
Fe[a]	100			
Co[b]		76	14	10
Ni[c]		96	2	2

[a] Reference 42. [b] Reference 40. [c] Reference 39.

of Ni(isobutene)$^+$ with a ratio of 92/8. The IRMPD results are summarized in Tables 1−4. The SORI for these three ions (Table 6, Figure 1 for cobalt) are in fair agreement with the IRMPD results.



(M = Fe, Co, Ni) (19)

$$CoC_4H_8^+ + nh\nu \longrightarrow CoC_4H_6^+ + H_2 \quad (67\%) \qquad (20)$$

$$CoC_2H_4^+ + C_2H_4 \quad (15\%) \qquad (21)$$

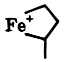
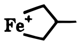
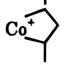
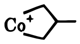
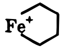
$$Co^+ + C_4H_8 \quad (18\%) \qquad (22)$$

$$Co^+ + n\text{-propane} \longrightarrow CoC_3H_6^+ + H_2 \qquad (23)$$

$$CoC_3H_6^+ + \text{isobutene} \longrightarrow \text{Co(isobutene)}^+ + C_3H_6 \qquad (24)$$

Some insight into the IRMPD behavior can be gained by examining the primary reactions of M$^+$ (M = Fe, Co, Ni) with isobutene (Table 7),[39,40,42] the CID of M(isobutene)$^+$ ion (Figures 2 and 3), and the mechanism of decomposition of M(isobutene)$^+$ (Scheme 2).[40] In contrast to the 1,3- elimination in the dehydrogenation process of group 3 metal ions (Sc$^+$, Y$^+$, La$^+$) with isobutene to produce a trimethylenemethane−metal ion,[55,56] it has been shown that Co$^+$ and Ni$^+$ dehydrogenate isobutene to generate butadiene−metal complexes.[39,40] CID of M(isobutene)$^+$ yielded loss of the whole ligand at all CID energies for iron, while losses of H$_2$ and C$_4$H$_8$ were observed for cobalt (Figure 2) and nickel (Figure 3). In addition, loss of C$_2$H$_4$ was also observed for cobalt as a minor product (less than 8%).[57] Interestingly, while loss of H$_2$ competes favorably with loss of C$_4$H$_8$ at low energy for nickel, loss of C$_4$H$_8$ is always dominant for cobalt. The reasons for these differences are discussed below.

Table 8. Thermochemical Estimates Used in Constructing Energy Diagrams and Estimating Reaction Enthalpies at 298 K

Species[a]	D°$_{298}$ (kcal/mol)	References
Fe$^+$-H	49.8 ± 1.4	32
Co$^+$-H	46.6 ± 1.4	32
Fe$^+$-CH$_2$	82 ± 5	32
Co$^+$-CH$_2$	84 ± 4	32
Co$^+$-CHCH$_3$	86[b]	
Fe$^+$-CH$_3$	58 ± 2	32
Fe$^+$-C$_2$H$_4$	39 ± 5	61
Co$^+$-C$_2$H$_4$	46 ± 8	43
Fe$^+$-(propene)	41 ± 5	61
Co$^+$-(propene)	48 ± 3	43
Fe$^+$-C$_4$H$_8$	44[c,d]	
Co$^+$-C$_4$H$_8$	49[d]	43
(C$_4$H$_8$ = 1-butene, *cis*-2-butene, *trans*-2-butene, isobutene)		
Fe$^+$—1,3-butadiene	48 ± 5	64
Co$^+$—1,3-butadiene	56	43
Fe$^+$-C$_4$H$_7$	58[e]	
Co$^+$-C$_4$H$_7$	63[f]	
C$_4$H$_7$ = methallyl, 2-methallyl		
 or 	91[g]	
 or 	87[h]	
	93[i]	

[a] Organic, radical and other ionic thermochemical data are taken from refs 65−69. [b] It is assumed that $D°_{298}$ (Co$^+$ −CHCH$_3$) is slightly higher than that of Co$^+$−CH$_2$, which is 84 ± 4 kcal/mol (ref 32). [c] Estimated on the basis of the trend observed for the M$^+$−alkene (M = Fe, Co, Ni) bond energies (refs 43, 61, 70). [d] It is assumed that for M$^+$−C$_4$H$_8$ (M = Fe, Co, Ni), the isomers of C$_4$H$_8$, namely 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutene, have similar bond strengths to the metal center. [e] It is assumed that $D°_{298}$ (Fe$^+$−C$_4$H$_7$) is slightly higher than $D°_{298}$ (Fe$^+$−C$_3$H$_5$), which is 56 kcal/mol (ref 42). [f] It is assumed that $D°_{298}$ (Co$^+$−C$_4$H$_7$) is slightly higher than $D°_{298}$ (Co$^+$−C$_3$H$_5$). $D°_{298}$ (Co$^+$−C$_3$H$_5$), in turn, is assumed to be >62 kcal/mol based on the exothermicity of the reaction $CoCH_3^+ + C_3H_8 \rightarrow CoC_3H_5^+ + CH_4 + H_2$ (Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3891). This value is obtained by using $D°_{298}$ (Co$^+$−CH$_3$) as 51 ± 4 kcal/mol (ref 32), $\Delta H_f°$ (CH$_3$) as 35.1 kcal/mol (ref 68), and $\Delta H_f°$ (C$_3$H$_5$) as 39.1 kcal/mol (ref 68). [g] It is assumed that $D°_{298}$ ironamethylcyclobutane is slightly higher than that of ironacyclobutane, which is 90 ± 5 kcal/mol (ref 61). [h] It is assumed that $D°_{298}$ cobaltamethylcyclobutane is slightly higher than that of cobaltacyclobutane, which is 86 ± 5 kcal/mol (ref 61). [i] It is assumed that $D°_{298}$ ironacyclopentane is a few kcal/mol higher than that of ironacyclobutane, which is 90 ± 5 kcal/mol (ref 61).

Fe(isobutene)$^+$. The loss of C$_4$H$_8$, exclusively, in the infrared activation of Fe(isobutene)$^+$ is in accordance with the absence of neutral loss products in the reaction of Fe$^+$ and isobutene (Table 7) and the CID results. The energy diagram for the decomposition of Fe(isobutene)$^+$ based on Scheme 2 is shown in Figure 4. Since C$_4$H$_8$ is lost exclusively for iron (a direct cleavage process), whereas for cobalt and nickel the loss of other products (rearrangement processes) were observed, clearly for iron the activation barriers for the loss of other products are either higher or close to the Fe$^+$−isobutene dissociation limit.

---

(55) Lech, L. M.; Freiser, B. S. *Organometallics* **1988**, *7*, 1948.

(56) Huang, Y.; Wise, M. B.; Jacobson, D. B.; Freiser, B. S. *Organometallics* **1987**, *6*, 346.

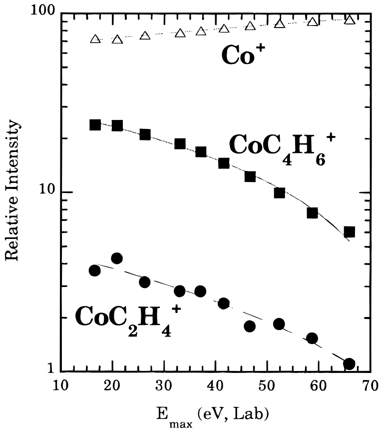


Figure 2. CID of Co(isobutene)$^+$ from the reaction of Co$^+$ with isobutane.

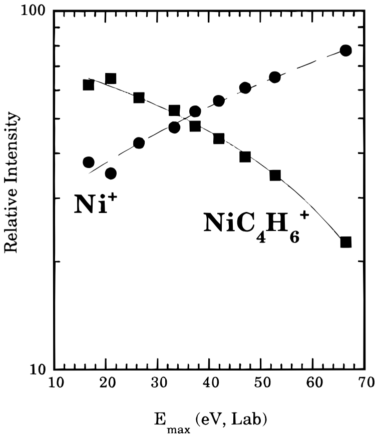
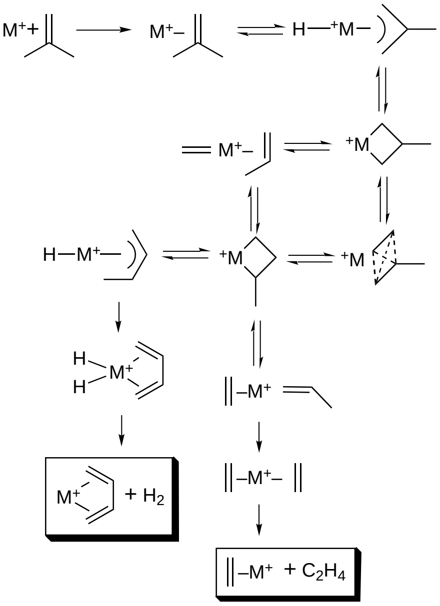


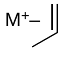
Figure 3. CID of Ni(isobutene)$^+$ from the reaction of Ni$^+$ with isobutane.

Scheme 2. Mechanism of Reaction for the Decomposition of M(isobutene)$^+$ To Produce MC$_2$H$_4$$^+$ and MC$_4$H$_6$$^+$ [a]

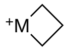


[a] Adapted from ref 40.

The kinetics dictate that when competitive channels are being accessed by infrared activation, direct cleavage is favored over rearrangement when these channels have equal activation barriers, and in some cases even when the rearrangement barrier is somewhat lower, depending on the *A* factor for these processes. In an analogous system, it has been suggested that the conversion from Fe(propene)$^+$ **5** to ironacyclobutane ion **6** proceeds through significant barriers.[58,59] Even though these barriers are high, Beauchamp and co-workers suggested that they are still below the M$^+$–propene dissociation limit.[59] In our system, even if infrared laser irradiation could increase the internal energy of the ion **4** so that it was converted to ironacyclobutane **7**, the barrier between **7** and propene carbene **8** must inhibit dehydrogenation to produce a butadiene complex (Figure 4). When compared to its cobalt or nickel analog, the nature of the ironacyclobutane structure,[60] the low Fe$^+$–alkene[43,61] and Fe$^+$–CH$_2$ [32] bond energies and high activation barrier between **7** and **8** could contribute to the observation of loss of the whole ligand, exclusively, only in the IRMPD of Fe(isobutene)$^+$.



5



6

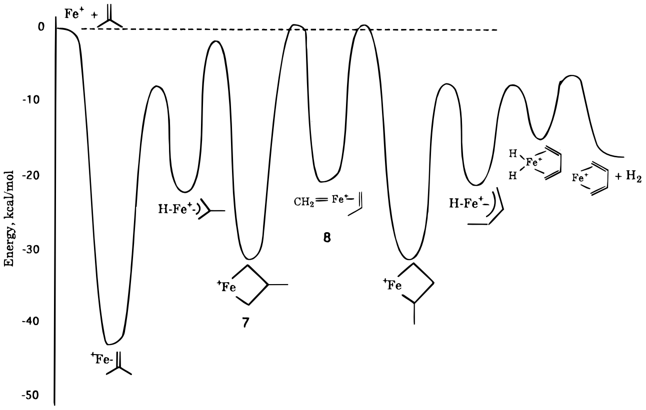


Figure 4. The potential energy diagram for the decomposition of Fe(isobutene)$^+$. High activation barriers prevented the formation of Fe(1,3-butadiene)$^+$.

Co(isobutene)$^+$ and Ni(isobutene)$^+$. The well-accepted mechanism of dehydrogenation of MC$_4$H$_8$$^+$ from the reaction of M$^+$ with isobutane (M = Fe, Co, Ni), [40] as well as the observed ligand displacement, reactions 23 and 24, rule out the possibility of irradiating a mixture of isomers in MC$_4$H$_8$$^+$ from the reaction of M$^+$ with isobutane. Therefore, observation of multiple products must come from similar activation barriers. As shown in Figure 5 for cobalt, which is also applicable for nickel, the two reaction channels (loss of H$_2$ and loss of C$_2$H$_4$) share common activation barriers up to the intermediate metallacyclobutane **9**.

The greater abundance of MC$_2$H$_4$$^+$ ion for cobalt than that for nickel is in agreement with CID and reactivity studies. The CID of Co(isobutene)$^+$ contains CoC$_2$H$_4$$^+$ as a minor product (less than 8%), while the CID of Ni(isobutene)$^+$ does not (Figures 2 and 3). Also, the reaction of M$^+$ with isobutene produces a greater abundance of MC$_2$H$_4$$^+$ for M = Co than

---

(57) Previously (ref 34), it was reported that the CID of M(isobutene)$^+$ (M = Fe, Co, Ni) yielded loss of the whole ligand for these three ions. Most likely, the other products, loss of H$_2$ and C$_2$H$_4$, were simply overlooked.

(58) Jacobson, D. B.; Freiser, B. S. *Organometallics* **1984**, *4*, 513.

(59) van Koppen, P. A. M.; Jacobson, D. B.; Illies, A.; Bowers, M. T.; Hanratty, M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 1991.

(60) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1982; Vol. 8, p 533.

(61) van Koppen, P. A. M.; Bowers, M. T.; Beauchamp, J. L.; Dearden, D. V. In *ACS Symposium Series: Bonding Energetics in Organometallic Compounds*; Marks, J. T., Ed.; American Chemical Society: Washington, DC, 1990; No. 428, Chapter 3, p 34.

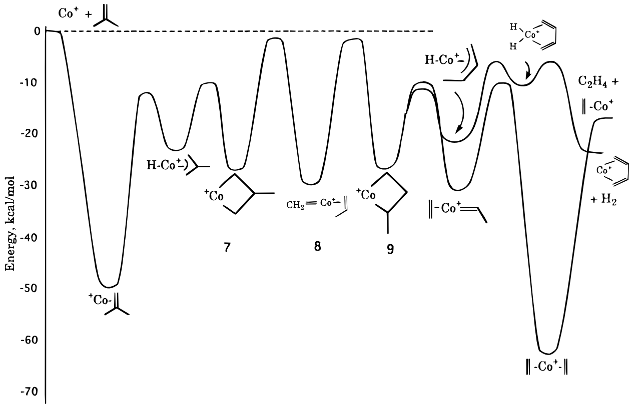


Figure 5. The potential energy diagram for the decomposition of Co(isobutene)$^+$. Infrared activation of this ion yields three product ions: Co^+, $CoC_2H_4^+$, and $CoC_4H_6^+$.

that for M = Ni (Table 7). A possible explanation for the greater abundance of $CoC_2H_4^+$ compared to $NiC_2H_4^+$ is that the overall activation barrier differences that lead to the formation of M(butadiene)$^+$ and M(ethene)$^+$ are somewhat larger for cobalt than for nickel.

IRMPD yields more dehydrogenation than loss of C_2H_4 for both cobalt and nickel. This fact correlates with thermochemical calculations which show that $MC_4H_6^+$ lies below $MC_2H_4^+$ in the potential energy diagram for both ions.[62]

Finally, for Co(isobutene)$^+$, loss of the whole ligand is observed in the IRMPD, while for nickel, it is not. This observation is in agreement with the CID studies (Figure 2). The difference between cobalt and nickel in this situation suggests that the activation barrier between **7** and **8** or between **8** and **9** lies closer to the metal−isobutene dissociation limit for cobalt than that for nickel (Figure 5). Such a case could arise as a result of the difference in metal−ligand bond strength or simply the difference in activation height.

$MC_5H_{10}^+$. As mentioned above, M^+ reacts with *n*-pentane to generate $MC_5H_{10}^+$ in the form of the bis(alkene) complex **1** for cobalt and the 1-pentene complex for iron; however, Fe(1-pentene)$^+$ easily rearranges to produce **1** also upon activation. Therefore, it is not surprising that the IRMPD of these ions yields loss of C_2H_4, exclusively, since the barrier to rearrangement lies below cleavage of the whole ligand and the smaller alkene is bound less strongly to the metal center than the larger alkene (reaction 25).[34] The photodissociation efficiencies for iron, cobalt, and nickel are comparable. In contrast to the

$$MC_5H_{10}^{\ +} + nh\nu \rightarrow MC_3H_6^{\ +} + C_2H_4 \qquad (25)$$

$$(M = Fe, Co, Ni)$$

IRMPD results, but not surprisingly, the CID of these ions produced loss of C_2H_4, C_3H_6, and C_5H_{10}.[34] Finally, SORI of these ions are in excellent agreement with the IRMPD results.

Correlation between IRMPD Results and the Infrared Spectra of the Parent Molecules. Of the ions studied here, $MC_2H_2^+$ and $MC_nH_{2n}^+$ (M = Fe, Co, Ni; $n = 2-5$), all are photoactive at 944 cm^{-1}, except $MC_2H_2^+$ and $NiC_2H_4^+$. The neutral organic molecules (C_2H_4, C_3H_6, 1-butene, *trans*-2-butene, and 1-pentene) absorb moderately at 944 cm^{-1}, except for *cis*-2-butene which has a weak absorption and acetylene, isobutene, and cyclopentane which have no absorption at that wavelength.[63] These data suggest that lack of absorption in the neutral spectra does not necessarily cause the metal-containing ions to be transparent. It has been pointed out that the strong interaction that exists between a metal ion and a ligand can perturb the vibrational frequencies of the ligand in the complex and that several conformations are possible for a complex ion.[25] In addition, each metal ion may yield different conformations of the resulting complex. These factors may account for the dissociation for these transition metal ions or lack thereof (e.g., the absence of absorption by $NiC_2H_4^+$) even in the case where the neutral molecules absorb weakly (*cis*-2-butene) or do not absorb at all (acetylene, isobutene, and cyclopentane).[25] The above factors may also explain why some ions dissociate more readily than others as exemplified by Co(butenes)$^+$ *vs* Ni(butenes)$^+$ and by $FeC_3H_6^+$ *vs* $NiC_3H_6^+$.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-FG02-87ER13766) for supporting this research and to the National Science Foundation (CHE-9224476) for supporting FTICRMS instrumentation. The authors also thank Dr. Yongqing Huang for helpful discussions.

JA943733Q

---

[62] The reactions of Co^+ + isobutene → $CoC_4H_6^+ + H_2$ and Co^+ + isobutene → $CoC_2H_4^+ + C_2H_4$ are exothermic by 24.7 and 16.8 kcal/mol, respectively. See Table 8 for thermochemical data. The results for nickel are similar.

[63] *The Aldrich Library of FT-IR Spectra, Vapor Phase*, 1st ed.; Pouchert, C. J., Ed.; Aldrich Chemical Co., Inc.: Milwaukee, WI, 1989; Vol. 3.

[64] Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086.

[65] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas-Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

[66] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.

[67] *CRC Handbook of Chemistry and Physics*, 72th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1991−1992.

[68] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[69] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1.

[70] Bauschlicher, C. W.; Partridge, H.; Langhoff, S. R. Submitted for publication.