Reactions of Group 8 Transition-Metal Ions (Fe^+, Co^+, and Ni^+) with Cyclic Hydrocarbons in the Gas Phase

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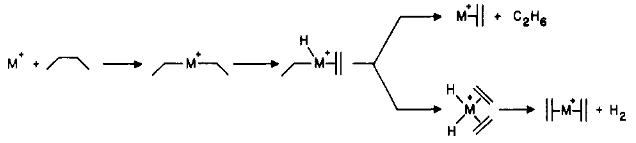
Abstract: The gas-phase reactions of group 8 transition-metal ions (Fe^+, Co^+, and Ni^+) with cyclic hydrocarbons were studied by Fourier transform mass spectrometry. Product structures were probed by using collision-induced dissociation (CID) and H/D exchanges. All three metal ions react with cyclobutane to generate ring-cleavage products exclusively. This is in contrast to reactions with cyclopentane and cyclohexane, where dehydrogenation dominates, producing cycloalkene- and cycloalkadiene-metal ion complexes. Bis(ethene)-metal ion complexes, formed in secondary reactions, are shown not to be in equilibrium with metallacyclopentanes. Metallacyclopentanes decompose by symmetric ring cleavage, producing an ethene-metal ion complex, or by an initial 1,3-hydrogen shift, producing a linear butene complex which dehydrogenates, forming a butadiene-metal ion complex. Both $Fe\text{-}c\text{-}C_5H_6^+$ and $Co\text{-}c\text{-}C_5H_6^+$ undergo six H/D exchanges with D_2. The rate constant for the first exchange is found to be about an order of magnitude faster than for the second exchange. Cycloalkadiene products of Fe^+ and Co^+ react rapidly with their corresponding cyclic-alkane analogues exclusively by multiple dehydrogenations. Cycloalkadiene products of Ni^+, however, were found to be unreactive with cyclic alkanes.

Gas-phase organometallic chemistry of transition-metal ions has proven to be both rich and unusual, with oxidative addition across carbon-halogen,[1-3] carbon-oxygen,[2,4,5] carbon-hydrogen,[2,6-9] and carbon-carbon bonds[2,6-9] observed. Determination of reaction mechanisms is a major thrust in these studies. Determination of ion product structures by using collision-induced dissociation,[6b,9] specific ion-molecule reactions,[9,10] and labeled compounds[10] has greatly facilitated the elucidation of reaction mechanisms. Thermochemistry of metal-methyl and metal-hydrogen ion complexes obtained with an ion beam instrument has also proved invaluable in postulating reasonable reaction mechanisms.[7,11]

Reactions with hydrocarbons are fundamentally important since only two types of bonds are available for metal insertion: C-H and C-C bonds. Transition-metal ions react with hydrocarbons, producing both dehydrogenation and alkane elimination products. Two simple mechanisms have been postulated to explain these results. Dehydrogenation of hydrocarbons may involve initial insertion of the metal ion into a C-H bond followed by a β-hydride shift, resulting in reductive elimination of hydrogen, producing an olefin-metal complex. Oxidative addition of a metal ion across a C-C bond is proposed as the initial step in cleavage of hydrocarbons. This is followed by a β-hydride shift across the metal with subsequent elimination of an alkane, again generating an olefin-metal ion complex. Detailed studies on Fe^+, Co^+, and Ni^+ indicate that an additional mechanism is also involved in their dehydrogenation reactions of linear alkanes larger than propane.[9,10] It was found that dehydrogenation can occur via initial insertion not only into C-H bonds but into internal C-C bonds as well. In fact this is the dominant mechanism for Co^+ and Ni^+. This initial insertion across a C-C bond can be followed by two successive β-hydride shifts onto the metal, with reductive elimination of hydrogen producing a bis(olefin)-metal complex (Scheme I). This mechanism requires that β-hydride shifts be competitive with alkane elimination. Both Ni^+ and Co^+ were observed to dehydrogenate linear alkanes larger than propane nearly exclusively via the 1,4-elimination process, with both C-H and C-C bond insertions leading to dehydrogenation products for Fe^+. These results clearly demonstrate that the simplest and most appealing mechanisms may not always be involved in product formation.

Scheme I



Here, we study in detail the reactions of the group 8 metal ions (Fe^+, Co^+, and Ni^+) with cyclic hydrocarbons. Although reactions of cyclic alkanes have been studied previously for Fe^+ [8a] and Co^+,[12] no structural studies were performed. In this paper, structures of product ions are probed by CID,[6b,9,13] specific ion-molecule reactions,[9,10] and H/D exchanges[8b,14,15] using deuterium. Mechanisms are then postulated based on these results. The high fraction of dehydrogenation vs. C-C bond cleavage products for cyclic hydrocarbons is interesting since these metal ions yield predominantly C-C cleavage products in reactions with aliphatic hydrocarbons.

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer previously described in detail[16] and equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell was constructed in our laboratory and includes a $^1/_4$-in.-diameter hole in one of the transmitter plates, which permits irradiation with various light sources. High-purity foils of the appropriate metals were attached to the opposite transmitter plate. Metal ions are generated by focusing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto the metal foil. Details of the laser ionization technique have been described elsewhere.[5,8]

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze-pump-thaw cycles to remove noncondensable gases. Deuterated cyclopentanone-$\alpha,\alpha,\alpha',\alpha'$-$d_4$ was syn-

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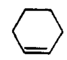
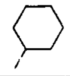
Table I. Percentages of Neutrals Lost in the Primary Reactions of Fe^+, Co^+, and Ni^+ with Cyclic Hydrocarbons

cyclic hydrocarbon	M^+	neutrals lost										
		H_2	$2H_2$	$3H_2$	CH_4	H_2, CH_4	$2H_2$, CH_4	C_2H_4	C_2H_6 (H_2 + C_2H_4)	C_3H_6	C_3H_8 (H_2 + C_3H_6)	C_4H_8
	Fe	5						95				
	Co	80						20				
	Ni	30						70				
	Fe	65	34					1				
	Co	22	20		2			47		9		
	Ni	57	13					27		3		
	Fe	100										
	Co	100										
	Ni	100										
	Fe	63	24	13								
	Co	33	37	7		1		1	1	20		
	Ni	65	25							10		
	Fe		100									
	Co		98					2				
	Ni	19	69					12				
	Fe	21	18	29	2	6	24					
	Co	7	9	13	7	31	27			3	2	1
	Ni	6	4	2	15	54	9			6	3	1

thesized according to the procedure of McNesby, Drew, and Gordon[17] by refluxing 9.0 mL of the ketone in the presence of 10.0 mL of D_2O containing 0.1 g of K_2CO_3 for 8–16 h in a closed system. Saturation of the water layer with K_2CO_3 is then followed by separation of the ketone layer, and the procedure is repeated 6 times. Mass spectrometric analysis showed about 94% cyclopentanone-$\alpha,\alpha,\alpha',\alpha'$-$d_4$ and 6% cyclopentanone-α,α,α'-d_3. Sample pressures were on the order of 1×10^{-7} torr. Argon was used as the collision gas for the CID experiments at a total sample pressure of approximately 5×10^{-6} torr. A Bayard–Alpert ionization gauge was used to monitor pressure.

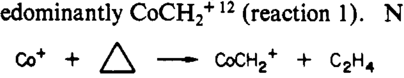
Details of the CID experiments have previously been discussed.[9,16,18] The collision energy of the ions can be varied (typically between 0 and 100 eV), from which plots of CID product ion intensities vs. kinetic energy can be made. These plots are reproducible to ±5% absolute and are informative, yielding additional structural information. The spread in ion kinetic energies is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.[19]

H/D exchanges were carried out by using deuterium at a pressure of (1–9) $\times 10^{-6}$ torr. Secondary reactions of the ions undergoing H/D exchanges complicated the interpretation. Addition of the hydrocarbon reactant through a pulsed valve alleviated this problem since no further reaction with the hydrocarbon neutral was observed after a 300-ms interaction time. Hence, the H/D exchanges could then be studied vs. time without loss of the product ion due to competing reactions. Pulsed-valve addition of reagent gases as applied to FTMS has been described in detail.[20]

Secondary reaction pathways were studied by using both continuous ejection and swept double-resonance ejection techniques.[21]

Results and Discussion

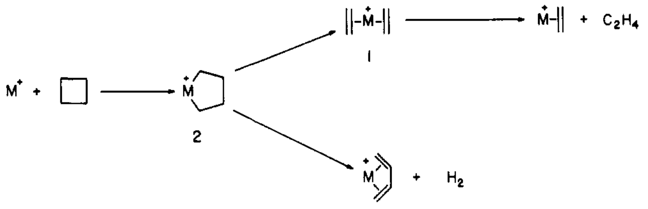
Reactions with Cyclopropane and Cyclobutane. Using an ion beam instrument, Beauchamp et al. reported that Co^+ undergoes an endothermic reaction with cyclopropane at 1-eV kinetic energy, producing predominantly $CoCH_2^+$[12] (reaction 1). No reactions



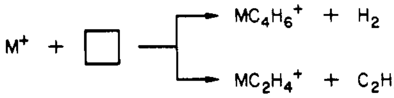
(1)

were observed for laser-desorbed Fe^+, Co^+, and Ni^+ with cyclopropane. Reaction 1 is roughly 7 kcal/mol endothermic for Co^+ and Ni^+, with Fe^+ being essentially thermoneutral.[22] The absence of reactivity toward cyclopropane is consistent with selecting laser-formed metal ions with little or no electronic or kinetic excitation.

Scheme II



Fe^+, Co^+, and Ni^+ react readily with cyclobutane, generating $MC_4H_6^+$ and $MC_2H_4^+$ products (reactions 2 and 3) (see Table I).



(2)
(3)

$CoC_4H_6^+$, generated in reaction 2, reacts rapidly with cyclobutane, forming $Co(C_4H_6)_2^+$ (reaction 4). Both $FeC_4H_6^+$ and

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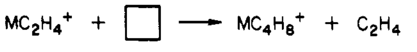
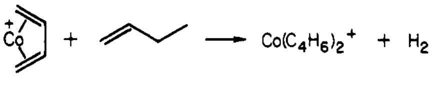
$NiC_4H_6^+$ are unreactive with cyclobutane. The product of reaction 3 reacts readily with cyclobutane to generate $MC_4H_8^+$ ions (reaction 5).



(5)

Only direct cleavage of C_4H_6 was observed in the CID spectra of $MC_4H_6^+$ ions generated in reaction 2. In addition, the CID spectra for $Co(C_4H_6)_2^+$ generated in reaction 4 are identical (same peaks, intensities, and energy dependence, within experimental error) with that obtained for CID of $Co(C_4H_6)_2^+$ generated by reaction 6. These results provide evidence for formation of



(6)

butadiene–metal ion complexes instead of cyclobutene–metal ion complexes in reaction 2. The CID spectra of $MC_4H_8^+$ ions produced in reaction 5 consist of C_2H_4 loss as the only fragmentation at low kinetic energy, with loss of C_4H_8 occurring at

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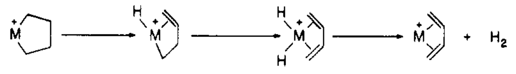
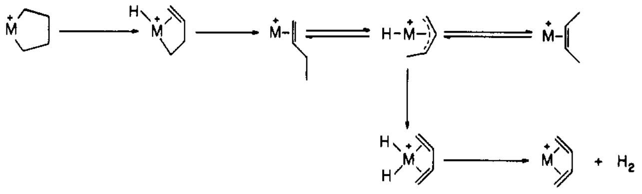
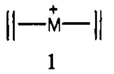
Scheme III



Scheme IV



higher kinetic energy. These results indicate the formation of bis(ethene)-metal ion complexes,[9] **1**, in reaction 5.



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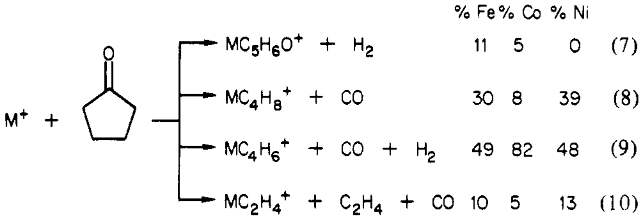
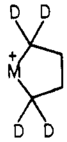
A mechanism for the formation of the products for the primary reactions with cyclobutane is presented in Scheme II. Initially, the metal ion oxidatively inserts into a C–C bond, generating a metallacyclopentane intermediate, **2**. The metallacyclopentane then decomposes either by symmetric ring cleavage, resulting in loss of ethene, or by dehydrogenation, producing a butadiene–metal ion complex. Metallacyclopentanes have been reported to decompose in solution by symmetric ring cleavage, resulting in formation of ethene, by β-hydride elimination, producing butene, and by reductive elimination of cyclobutane.[23-25] In addition, decomposition of metallacyclopentanes has also been studied theoretically.[26] Stable metallacyclopentanes have been synthesized by decarbonylation of cyclopentanone in the gas phase by Fe^+, Co^+, and Ni^+ along with three other products (reactions 7–10).[9]



The metallacyclopentanes produced in reaction 8 decompose by both symmetric ring cleavage and dehydrogenation.[9] The product of reaction 9 is probably formed by initial loss of CO, generating metallacyclopentane, followed by dehydrogenation, producing a butadiene–metal ion complex.

Dehydrogenation of metallacyclopentanes may simply involve two sequential hydride shifts as shown in Scheme III, or a 1,3-hydrogen shift may occur, generating a linear butene–metal ion complex which readily dehydrogenates as shown in Scheme IV. The mechanism for dehydrogenation of gas-phase metallacyclopentanes was probed by using cyclopentanone-α,α,α′,α′-d_4. Decarbonylation, reaction 8, then produces a deuterated metallacyclopentane, **3**. Formation of the butadiene–metal ion complex, as in reaction 9, generates products with varying degrees of deuteration, as shown in reactions 11–13. In addition, fragment ion abundances vs. ion kinetic energy for CID of $FeC_4H_4D_4^+$ (the stable metallacyclopentane, **3**) is shown in Figure 1. Dehydrogenation via loss of H_2, HD, or D_2 is observed along with loss of $C_2H_2D_2$. Similar results were obtained for CID on the $NiC_4H_4D_4^+$ metallacyclic species. Unfortunately, the intensity of the $CoC_4H_4D_4^+$ ion was too low for its CID spectra to be studied. These results indicate that dehydrogenation by Scheme IV occurs since dehydrogenation by Scheme III requires loss of H_2 exclusively. A possible complication in this study is that the metallacyclopentane may be in equilibrium with the bis(ethene) complex (eq 14). This equilibrium has been observed in solution.[27] In addition, metallacycles have been synthesized in solution by olefin dimerization reactions.[28] This equilibrium could easily account for the results in reactions 11–13 and also for the CID results. Bis(ethene)–metal ion complexes were generated in reaction 5 for Fe^+, Co^+, and Ni^+. C_2H_4 and C_4H_8 are the only fragments observed in the CID spectra of the bis(ethene) complexes. If the equilibrium in reaction 14 was occurring in the gas phase, then some dehydrogenation producing $MC_4H_6^+$ ions would be expected in the CID spectra but this is not observed. Exclusive loss of $C_2H_2D_2$ from the CID spectrum of the deuterated metallacyclopentane ion, **3**, is also consistent with this conclusion. Therefore, the deuterium losses in reactions 12 and 13 and in Figure 1 probably proceed via the 1,3-hydrogen shift mechanism



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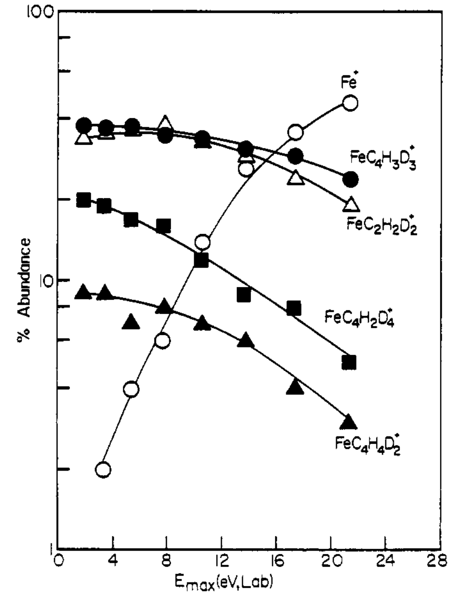
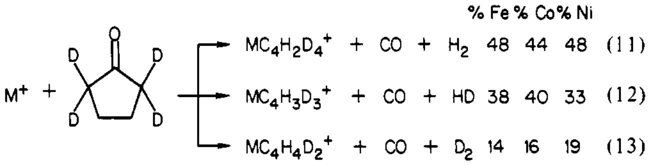


Figure 1. CID product ion abundances vs. kinetic energy for $FeC_4H_4D_4^+$ ions generated by decarbonylation of cyclopentanone-α,α,α′,α′-d_4 by Fe^+.



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Scheme V

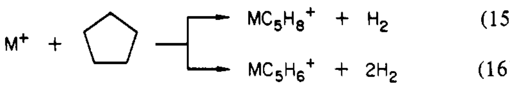
outlined in Scheme IV. Loss of H_2 in reaction 11 may, however, be occurring by either Scheme III or Scheme IV.

The fraction of dehydrogenation vs. ethene loss is quite variable for reactions of the three metal ions with cyclobutane (Table I). Both Fe^+ and Ni^+ show dominant ring-cleavage products while dehydrogenation dominates for Co^+. The high fraction of dehydrogenation for Co^+ is in accord with the results for reactions 8 and 9 and is consistent with β-hydride transfers being more facile for Co^+ than for either Fe^+ or Ni^+.[9] It is interesting that insertion into C–H bonds, while possible, is not necessary to explain the formation of the primary reaction products.

The reactivity of $MC_2H_4^+$ with cyclobutane is unexpected since metal–alkene complexes of Fe^+, Co^+, and Ni^+ are unreactive with aliphatic alkanes.[29] Again, insertion into a C–C bond is postulated as the initial process (Scheme V), generating an ethene–metallacyclopentane intermediate, **4**. Symmetric ring cleavage occurs, generating a tris(ethene)–metal complex, which eliminates ethene, forming the bis(ethene)–metal ion complex, **1**, as shown in Scheme V. Dehydrogenation generating an ethene–butadiene product or successive β-hydride shifts across the metal resulting in loss of ethane producing a butadiene–metal ion complex is not observed. This indicates that the presence of an olefin ligand greatly influences the decomposition of gas-phase metallacyclopentanes.

Reactions with Cyclopentane and Cyclopentene. Product distributions for the primary reactions of Fe^+, Co^+, and Ni^+ with cyclopentane and cyclopentene are listed in Table I. Dehydrogenation is essentially the only process observed for Fe^+ reacting with cyclopentane, with both dehydrogenation and C–C bond cleavage processes observed for Co^+ and Ni^+. The primary product distributions are in good agreement with those previously reported for Fe^+ (conventional ICR spectrometer)[8a] and for Co^+ (~1-eV kinetic energy, ion beam instrument).[12]

Dehydrogenation reactions 15 and 16 are observed for all three metal ions studied. The product of reaction 15 may consist of a 1,4-pentadiene–metal ion complex **5** or a cyclopentene–metal ion complex **6**. Loss of H_2 from CID of the product of reaction 15 is the only fragmentation observed at >90% yield for all three metal ions at low kinetic energy, with loss of C_5H_8 observed at higher kinetic energy. Only C–C bond cleavage products are observed in the CID spectra of (pentadiene)iron(+) products.[30] Therefore, Fe^+, Co^+, and Ni^+ dehydrogenate cyclopentane to generate a cyclopentene–metal ion complex, **6**, exclusively.



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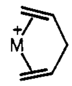

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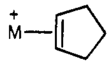


6

Dehydrogenation may occur by initial oxidative addition across a C–H bond, followed by a β-hydride transfer with subsequent reductive elimination of hydrogen (Scheme VI). Although this mechanism is plausible, a good case for initial C–C bond insertion can be made. First, oxidative addition of these metal ions across C–C bonds is thermally more favorable than oxidative addition across C–H bonds (Table II). Second, all three metal ions have been reported to dehydrogenate linear alkanes larger than propane by initial insertion into C–C bonds.[9,10] Third, all three metal ions dehydrogenate cyclobutane via initial insertion into C–C bonds, with no C–H bond insertion being observed as discussed above.

Scheme VI

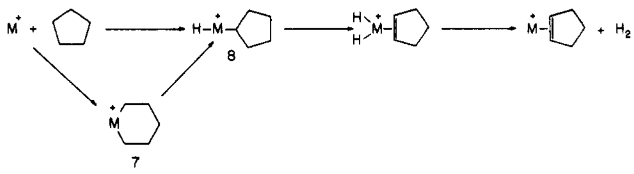
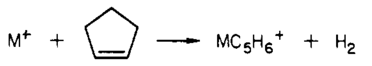


Table II. Bond Dissociation Energies (kcal/mol) for M^+-R Species

bond energy	Fe^+	Co^+	Ni^+
$D°(M^+–H)$	58 ± 5[a]	52 ± 4[b]	43 ± 2[c]
$D°(M^+–CH_3)$	69 ± 5[d]	61 ± 4[b]	48 ± 5[d]
$D°(M^+–H) + D°(M^+–CH_3)$	127	113	91
$2D°(M^+–CH_3)$	138	122	96

[a] Reference 11c. [b] Reference 7a. [c] Reference 7b. [d] Reference 11b.

Hence, an alternative dehydrogenation mechanism is presented in Scheme VI in which initial insertion into a C–C bond is proposed, generating metallacyclohexane intermediate **7**. This is followed by an α-hydride abstraction with concurrent regeneration of the 5-membered ring producing **8**. Dehydrogenation of **8** then occurs by β-hydride abstraction producing **6**. The cyclopentene–metal ion complex, **6**, can eliminate another H_2, producing $MC_5H_6^+$, provided it retains sufficient internal energy. That all three metal ions react with cyclopentene to generate $MC_5H_6^+$ exclusively (reaction 17) corroborates this assertion. Unfortunately, there is no way to distinguish between initial C–H or C–C bond insertion mechanisms.



(17)

The exothermicity of reactions 15 and 16 implies that $D°(M^+–c\text{-}C_5H_8) > 26$ kcal/mol and $D°(M^+–c\text{-}C_5H_6) > 50$ kcal/mol.[22] Reaction 16 was reported to be endothermic for Co^+ (ion beam instrument), in contrast to our findings.[12]

The nature of the M-c-$C_5H_6^+$ ions produced in reactions 16 and 17 is of particular interest. C_5H_6 is the only fragment observed in the FTMS-CID spectra at all kinetic energies studied for all three metal ions. However, CID of Fe-c-$C_5H_6^+$ in a sector instrument at 8 keV produces predominantly $FeC_5H_5^+$ and Fe^+ in roughly a 2:1 ratio.[31] Both Fe-c-$C_5H_6^+$ and Co-c-$C_5H_6^+$ undergo six H/D exchanges in the presence of excess deuterium, with no exchanges observed for Ni-c-$C_5H_6^+$. Six H/D exchanges have previously been reported for $CoC_5H_6^+$ ions produced by reaction with 1,5-norbornadiene.[15] Figure 2 shows the spectrum obtained when Co-c-$C_5H_6^+$ is trapped in the presence of $\sim 5 \times 10^{-6}$ torr D_2 for 5 s. The rate constants for the first and second H/D exchanges are listed in Table III. The first exchange is slow (about $^1/_{20}$ that of the Langevin collision rate) for both ions, but the second exchange is considerably slower than the first for both ions.

Scheme VII illustrates a proposed mechanism for the sequential H/D exchanges which invokes a rapid equilibrium between the cyclopentadiene complex, **9**, and the hydrido–cyclopentadienyl complex, **10**. The low-energy and high-energy CID results indicate that there is an equilibrium between the cyclopentadiene and hydrido–cyclopentadienyl species. Initially, oxidative addition of deuterium to **10** forms an activated complex which reductively eliminates HD, forming **11**. Although complexes **11** and **12** are in rapid equilibrium, the incorporated deuterium will remain unscrambled in the endo position. Complex **12** rearranges to **13** via a [1,5] sigmatropic shift (thermally allowed in the ground state[33]), which is known to occur rapidly at room temperature in labeled cyclopentadiene,[34] but which appears to be the rate-limiting

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[29] Jacobson, D. B.; Freiser, B. S., unpublished results.

[30] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

[31] Peake, D. A.; Gross, M. L.; Ridge, D. P., unpublished results.

[32] Gioumousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *29*, 294.

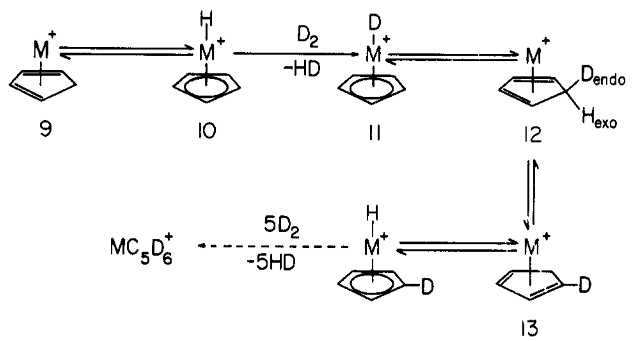
[33] Sprangler, C. W. *Chem. Rev.* **1976**, *76*, 187.

Table III. Rate Constants[a] for H/D Exchange with Co-c-$C_5H_6^+$ and Fe-c-$C_5H_6^+$

reaction	k		k_L[b]	
	Co^+	Fe^+	Co^+	Fe^+
M-c-$C_5H_6^+$ + D_2 → M-c-$C_5H_5D^+$ + HD	0.05 ± 0.03	0.06 ± 0.03	1.05	1.04
M-c-$C_5H_5D^+$ + D_2 → M-c-$C_5H_4D_2^+$ + HD	0.007 ± 0.004	0.002 ± 0.001	1.05	1.04

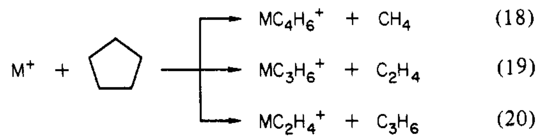
[a] All rate constants in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [b] Langevin polarization theory; see ref 32. The molecular polarizability of deuterium is given as 7.749 × 10^{-25} cm^3 in ref 32.

Scheme VII



step for the second and subsequent exchanges in the gas phase. This mechanism then accounts for the observed H/D exchanges for both Fe-c-$C_5H_6^+$ and Co-c-$C_5H_6^+$. The absence of H/D exchanges for Ni-c-$C_5H_6^+$ may be either due to a failure of D_2 to oxidatively add on Ni^+, perhaps because the process is endothermic, or due to the Ni-c-$C_5H_6^+$ complex being "frozen" as (cyclopentadiene)nickel(+).

In addition to dehydrogenation products, significant C–C bond cleavage products are also observed for Co^+ and Ni^+. Solution-phase studies on nickelacyclohexanes and titanacyclohexanes showed that they decompose by C–C bond cleavage, yielding predominantly ethene, some methane and butenes, and little or no propene.[35] Labeling studies indicated that α-C–C bond cleavage of the ring seemed to occur more often than β-C–C bond cleavage. Qualitatively, these same results are seen for Co^+ and Ni^+ in this study. A mechanism for formation of these C–C bond cleavage products has been described in detail for Co^+ by Beauchamp et al.[12] and is presented in Scheme VIII. As shown in Scheme VIII loss of methane, reaction 18, is proposed to proceed



by an initial α-C–C bond cleavage from **7** to form intermediate **14**. As discussed above for metallacyclopentane, two successive hydride transfers occur followed by reductive elimination of methane, producing a butadiene–metal ion complex. Loss of ethene, process 19, may occur by either α-C–C or β-C–C bond cleavage as shown in Scheme VIII. Reaction 20, loss of C_3H_6, presumably occurs via β-C–C bond cleavage. The exothermicity of reactions 19 and 20 implies $D°(M^+–C_3H_6)$ and $D°(M^+–C_2H_4)$ > 36 kcal/mol.[22]

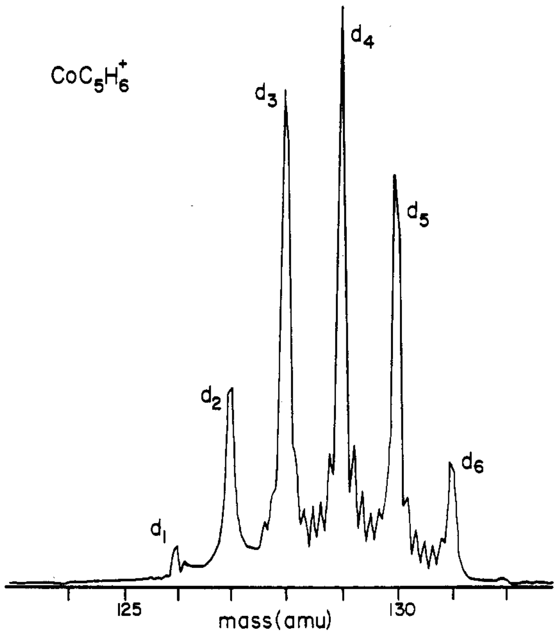
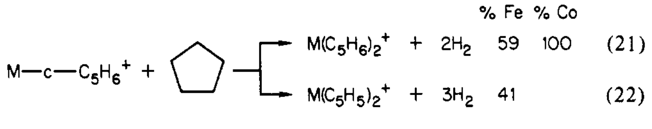


Figure 2. Mass spectrum obtained when Co-c-$C_5H_6^+$, generated by reacting Co^+ with cyclopentene (pulsed into the instrument), is trapped in the presence of 1 × 10^{-6} torr D_2 for 5 s.

We would like to put forth an alternative mechanism for the losses of CH_4, C_2H_4, and C_3H_6 which invokes an initial β-hydride abstraction of **7** producing **15** (Scheme IX). This hydride may then transfer to the carbon bound directly to the metal (a 1,4 hydrogen-atom shift), generating a 1-pentene–metal ion complex, **16**. This is analogous to the mechanism observed for dehydrogenation of metallacyclopentane presented in Scheme IV. Decomposition of (olefin)metal(+) complexes has been studied recently in the gas phase by both ion–molecule reactions[9,30,36] and CID.[9,30] In these studies, oxidative addition of an allylic C–C bond or a terminal C–C bond is postulated to occur initially for 1-pentene, generating complexes **17** and **18** in Scheme IX, respectively. β-Hydride shifts result in formation of a bis(olefin) complex, **19**, in the former and a butadiene complex (CH_4 loss) in the latter. The bis(olefin) complex then eliminates either of the olefins as shown in Scheme IX. This mechanism is particularly appealing since the product ratios for loss of CH_4, C_2H_4, and C_3H_6 are in excellent agreement with results for CID of 1-pentene bound to either Co^+ or Ni^+ [9,30] and for reactions of Co^+ and Ni^+ with 1-pentene.[9,30,36] An interesting observation in this study is that elimination of H_2 by intermediate **15** to produce an aliphatic alkadiene–metal ion complex is not observed.

Fe-c-$C_5H_6^+$ and Co-c-$C_5H_6^+$, produced in reactions 16 and 17, react rapidly with cyclopentane to generate dehydrogenation products exclusively (reactions 21 and 22). The products of



reaction 21 may consist of either $M(C_5H_5)(C_5H_7)^+$ or $M(C_5H_6)_2^+$. Ni-c-$C_5H_6^+$ is unreactive with cyclopentane. (Cyclopentadienyl)nickel(+), however, has been reported to dehydrogenate cyclic alkanes in the gas phase.[14] The complete absence of loss of just one H_2 to generate $M(C_5H_6)(C_5H_8)^+$ species indicates in this case that Fe-c-$C_5H_6^+$ and Co-c-$C_5H_6^+$ are more powerful dehydrogenating agents than their respective bare metal ions. The dominant process in the CID spectra of the products of reaction 21 is dehydrogenation producing metallocene ions, with small amounts of $MC_5H_6^+$, $MC_5H_5^+$, and M^+ also observed.

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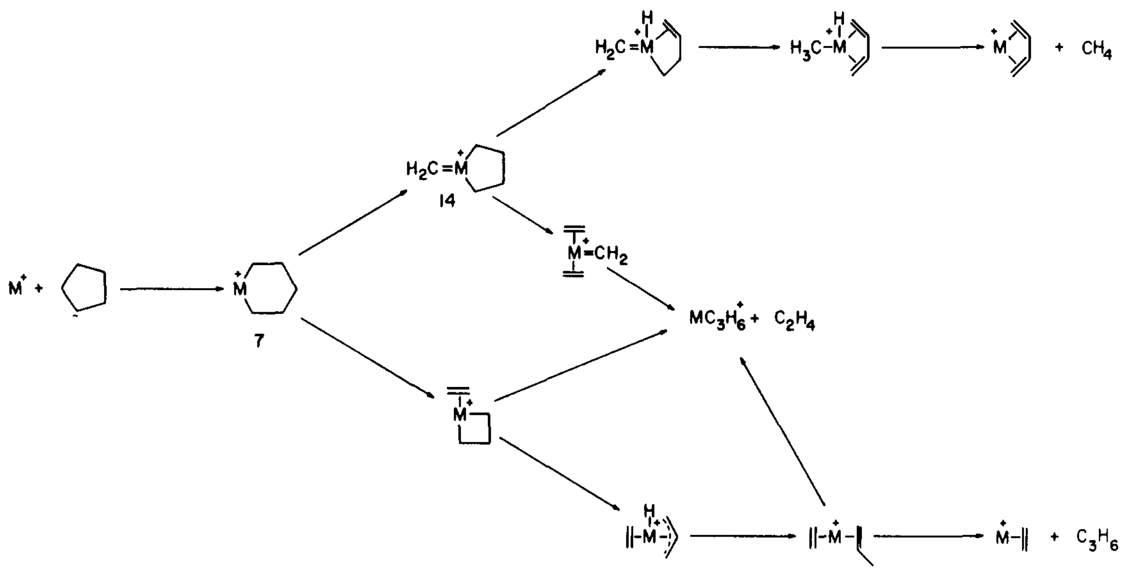
(34) (a) Roth, W. *Tetrahedron Lett.* **1964**, 1009. (b) Berson, J. A.; Aspelin, G. G. *Tetrahedron* **1964**, *20*, 2697 and references therein.

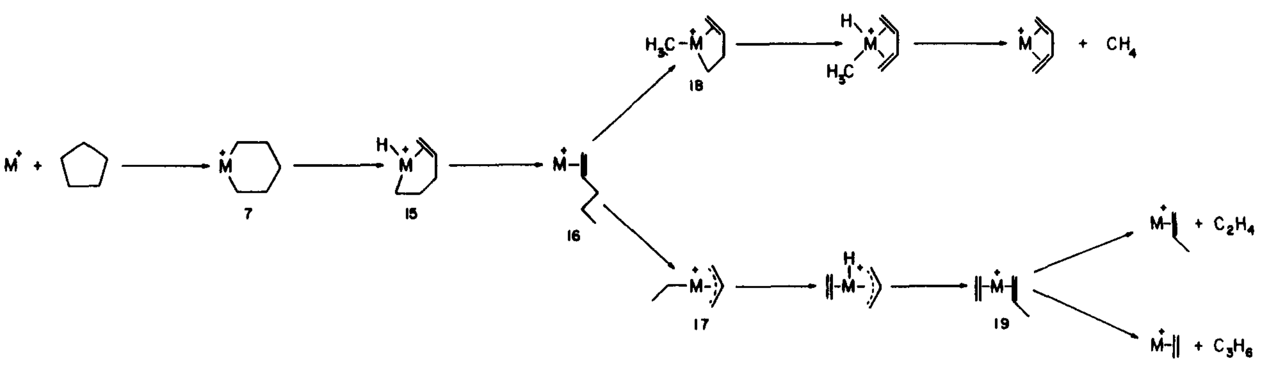
(35) (a) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7418. (b) Grubbs, R. H.; Miyashita, A. "Fundamental Research in Heterogeneous Catalysis"; Tsutsue, M., Ed.; Plenum Press: New York, 1979; Vol. 3, p 151.

(36) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624.

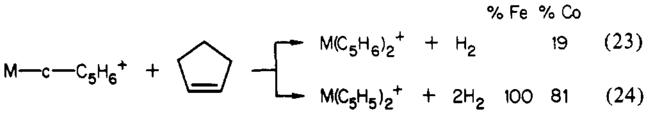
Scheme VIII



Scheme IX



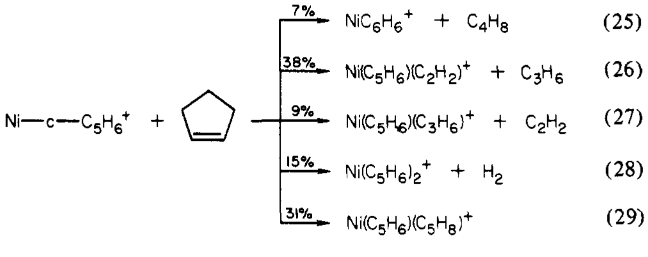
Reactions 23 and 24 were observed for M-c-$C_5H_6^+$ (M = Fe or Co) reacting with cyclopentene. CID of $M(C_5H_5)_2^+$ ions



$$\text{M–c–}C_5H_6^+ + \text{c-}C_5H_8 \rightarrow M(C_5H_6)_2^+ + H_2 \quad (\%\text{Fe } 19) \qquad (23)$$

$$\text{M–c–}C_5H_6^+ + \text{c-}C_5H_8 \rightarrow M(C_5H_5)_2^+ + 2H_2 \quad (\%\text{Fe } 100, \%\text{Co } 81) \qquad (24)$$

produced in reaction 24 yield losses of C_5H_5 and $2C_5H_5$ as the only fragmentations, which is consistent with metallocene formation.[37] In contrast to the above results, Ni-c-$C_5H_6^+$ reacts with cyclopentene to yield several ring-cleavage products in addition to dehydrogenation (reactions 25–29). The abundance



$$\text{Ni–c–}C_5H_6^+ + \text{c-}C_5H_8 \xrightarrow{7\%} NiC_6H_6^+ + C_4H_8 \qquad (25)$$

$$\xrightarrow{38\%} Ni(C_5H_6)(C_2H_2)^+ + C_3H_6 \qquad (26)$$

$$\xrightarrow{9\%} Ni(C_5H_6)(C_3H_6)^+ + C_2H_2 \qquad (27)$$

$$\xrightarrow{15\%} Ni(C_5H_6)_2^+ + H_2 \qquad (28)$$

$$\xrightarrow{31\%} Ni(C_5H_6)(C_5H_8)^+ \qquad (29)$$

of ring-cleavage products and the observation of the condensation process, reaction 29, are surprising since $NiCp^+$ (Cp = cyclopentadienyl) reacts with cyclic alkanes to generate dehydrogenation products exclusively.[14] Figure 3 shows a plot of CID fragment ion abundances vs. kinetic energy for $Ni(C_5H_6)(C_5H_8)^+$ ions generated in reaction 29. Ring-cleavage products (loss of C_3H_6 and C_4H_8) along with loss of C_5H_8 are observed. This is in accord with the ion–molecule reactions for Ni-c-$C_5H_6^+$ with cyclopentene. The absence of any C_2H_2 loss or dehydrogenation products in Figure 3, however, is not in accord with reactions 27 and 28 but such differences between CID and ion–molecule reactions, although not well understood, have been previously noted.[30]

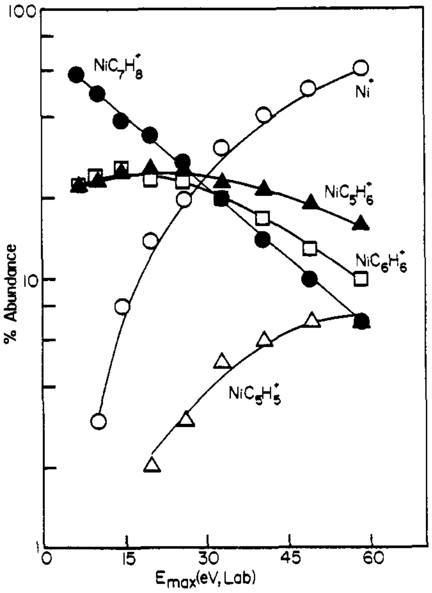


Figure 3. CID product ion abundances vs. kinetic energy for $Ni(C_5H_6)(C_5H_8)^+$ ions generated in reaction 29.

The kinetics of the H/D exchanges described earlier allows reactions of M-c-$C_5H_5D^+$ species to be readily studied. The

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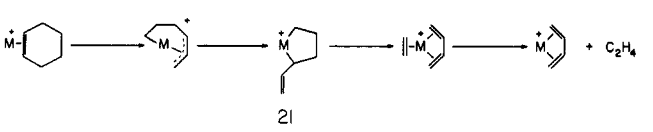
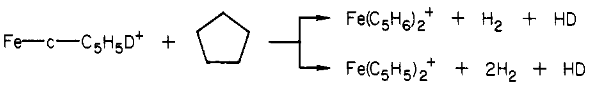
[37] Ferrocene and nickelocene cations lose C_5H_5 and $2C_5H_5$ as the only losses under CID conditions.

Scheme X



half-life for M-c-$C_5H_5D^+$ in the presence of ~1 × 10^{-6} torr D_2 is about 2 s. Hence, reactions of M-c-$C_5H_5D^+$, where the deuterium is in a unique and distinguishable position from the remaining five hydrogens (see Scheme VII), can be monitored. The time scale for studying this reaction is critical. The M-c-$C_5H_6^+$, and subsequently M-c-$C_5H_5D^+$, is generated by reacting the metal ion (Fe^+ or Co^+) with cyclopentene (pulsed into the instrument) in the presence of D_2 for 250 ms. The M-c-$C_5H_5D^+$ is then isolated by swept double-resonance ejection[21] and allowed to react with cyclopentane or cyclopentene for up to 250 ms. At longer reaction times, small amounts of multiple H/D exchanges occur which complicate interpretation of the results.

$FeC_5H_5D^+$ reacts with cyclopentane with nearly complete loss of the label (>95%) (reactions 30 and 31). $CoC_5H_5D^+$, on the other hand, reacts with cyclopentane with complete retention of the label (reaction 32). In addition, both $FeC_5H_5D^+$ and $CoC_5H_5D^+$ react with cyclopentene to generate $M(C_5H_5)_2^+$ species, with no $M(C_5H_4D)(C_5H_5)^+$ produced. This indicates that the deuterium has remained in a unique position without being scrambled with the hydrogens. The observation of reactions 30 and 31 for $FeC_5H_5D^+$ implies that the hydrido-cyclopentadienyl complex, **20**, is the reactive species, with the cyclopentadiene form being inert. If the (cyclopentadiene)metal(+) was the reactive species, then retention of the label, as seen for Co-c-$C_5H_5D^+$ in reaction 32, would be expected. Therefore, the cyclopentadiene form of Co-c-$C_5H_5D^+$ is postulated as the reactive species, with the hydrido-cyclopentadienyl species being unreactive. These unusual results warrant further study, which is currently underway.



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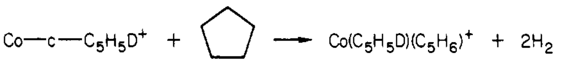

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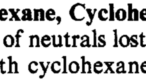

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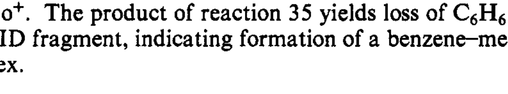
Reactions with Cyclohexane, Cyclohexene, and Methylcyclohexane. The distributions of neutrals lost in the primary reactions of Fe^+, Co^+, and Ni^+ with cyclohexane, cyclohexene, and methylcyclohexane are shown in Table I. The results for reactions of cyclohexane with Fe^+ and Co^+ are in good agreement with those previously reported.[8a,12] In general, the chemistry of cyclohexane parallels that for cyclopentane.

Dehydrogenation reactions 33–35 are the dominant processes observed for cyclohexane. CID of the products of reactions 33 and 34 generates $MC_6H_6^+$ ions in >80% yields at low kinetic energy for Fe^+ and Co^+. Only a trace of $MC_6H_8^+$ is seen in the CID spectra of $MC_6H_{10}^+$ (M = Fe, Co) at all kinetic energies studied. This is consistent with formation of cyclohexene- and 1,3-cyclohexadiene-metal ion products in reactions 33 and 34 for Fe^+ and Co^+. The product of reaction 35 yields loss of C_6H_6 as the only CID fragment, indicating formation of a benzene-metal ion complex.



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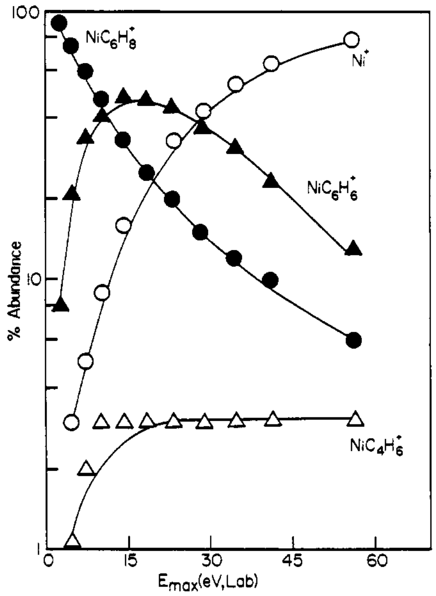
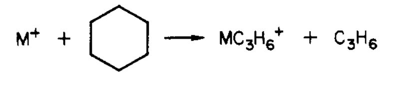


Figure 4. CID product ion abundances vs. kinetic energy for $NiC_6H_{10}^+$ ions generated in reaction 33.

CID of $NiC_6H_{10}^+$ ions generated in reaction 33 yields loss of H_2, $2H_2$ and C_2H_4. A plot of CID fragment ion abundances vs. kinetic energy for $NiC_6H_{10}^+$ is shown in Figure 4. A mechanism for loss of C_2H_4 in the CID spectra of $NiC_6H_{10}^+$ generated in reaction 33 is shown in Scheme X. Ni^+ initially inserts into the allylic C–C bond followed by rearrangement to a metallacyclopentane complex, **21**. Symmetric ring cleavage results in formation of a butadiene-ethene complex, which eliminates ethene. Dehydrogenation of **21** may also occur, producing a 1,3,5-hexatriene complex; however, a majority of the $NiC_6H_8^+$ is believed to consist of cyclohexadiene bound to Ni^+. CID of $NiC_6H_8^+$, generated in reaction 34, yields loss of H_2, generating $NiC_6H_6^+$ as the only fragmentation at low kinetic energy, with loss of C_6H_8 seen at high kinetic energy. The stability of (cyclohexadiene)nickel(+) indicates that a high activation barrier may exist for dehydrogenation to occur, producing $NiC_6H_6^+$ vs. the Fe^+ or Co^+ analogues.

The exothermicity of reactions 33–35 indicates that $D°(M^+\text{-c-}C_6H_{10}) > 28$ kcal/mol, $D°(M^+\text{-c-}C_6H_8) > 55$ kcal/mol, and $D°(M^+\text{-c-}C_6H_6) > 49$ kcal/mol.[22] The value for $D°(M^+\text{-c-}C_6H_6)$ only holds for Fe^+ and Co^+ since Ni^+ does not generate Ni-c-$C_6H_6^+$ from cyclohexane (Table I).

Fe^+ reacts with cyclohexene to yield $Fe(C_6H_6)^+$ exclusively, with this same product dominating for Co^+ and Ni^+. $NiC_6H_8^+$ and $NiC_4H_6^+$ as well as $CoC_4H_6^+$ are also observed (reactions 36 and 37). The product of reaction 37 is probably formed by the mechanism outlined in Scheme X and is further evidence for the formation of (cyclohexene)nickel(+) in reaction 33. The observation of reaction 36 is further evidence for the stability of (1,3-cyclohexadiene)nickel(+) complexes.



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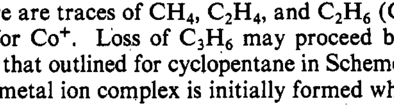
(37)

The C–C bond cleavage process, reaction 38, is observed for both Co^+ and Ni^+. The exothermicity of this reaction implies $D°(M^+\text{-}C_3H_6) > 39$ kcal/mol[22] for Co^+ and Ni^+. As shown in Table I, there are traces of CH_4, C_2H_4, and C_2H_6 (C_2H_4 + H_2) losses seen for Co^+. Loss of C_3H_6 may proceed by a process analogous to that outlined for cyclopentane in Scheme IX. Here, a 1-hexene-metal ion complex is initially formed which decomposes preferentially by insertion into the allylic C–C bond, resulting



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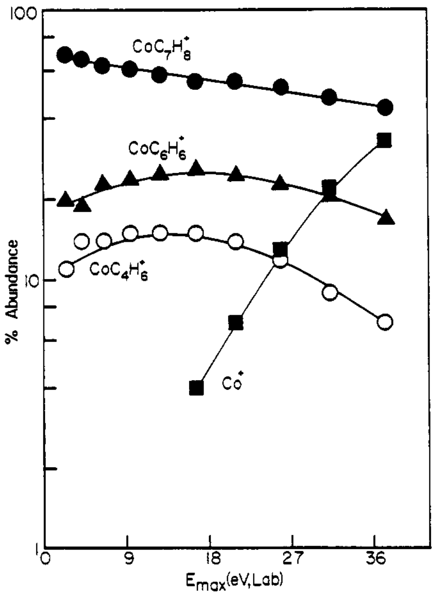
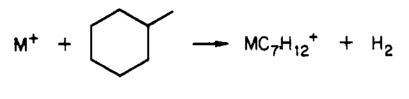


Figure 5. CID product ion abundances vs. kinetic energy for $Co(C_6H_8)(C_7H_{10})^+$ ions generated in reaction 43.

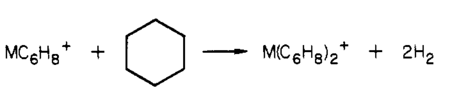
in generation of a bis(propene)-metal complex which then eliminates propene. Alternatively, processes similar to those presented in Scheme VIII may be involved.

Reactions with methylcyclohexane are dominated by dehydrogenations and methane loss accompanied by dehydrogenations (Table I). As with cyclopentane and cyclohexane, ring-cleavage products are also observed for both Co^+ and Ni^+. CID of both $CoC_7H_{12}^+$ and $FeC_7H_{12}^+$ formed in reaction 39 yields $MC_7H_8^+$

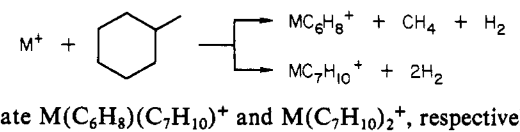

(39)

and $MC_6H_6^+$ ions in roughly a 5:1 ratio at all kinetic energies studied. A possible implication is that β-methyl shifts are competitive with β-hydride shifts for methylcyclohexenes. Hence, the CID results indicate that in the primary reactions of M^+ with methylcyclohexane (Table I) some methane loss may occur following dehydrogenation. A majority of methane loss, however, probably occurs via initial insertion into the methyl-ring C-C bond followed by β-hydride abstraction and elimination of methane.

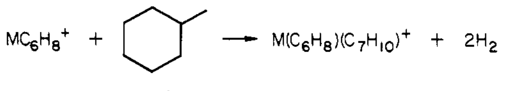
No secondary reactions were observed for Ni^+ complexes while cycloalkadiene products of both Fe^+ and Co^+ are reactive. The products of reaction 34, $FeC_6H_8^+$ and $CoC_6H_8^+$, react readily with cyclohexane to lose $2H_2$ (reaction 40). CID of the product of

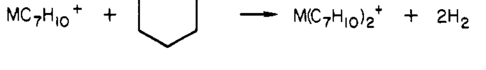

(40)

reaction 40 generates $MC_6H_6^+$ as the only fragment at low kinetic energy, with M^+ observed at high kinetic energy. No dehydrogenation producing $M(C_6H_6)(C_6H_8)^+$ or $M(C_6H_6)_2^+$ ions was observed. $MC_6H_8^+$ and $MC_7H_{10}^+$ (M = Fe and Co) generated in reactions 41 and 42 react readily with methylcyclohexane to


(41)
(42)

generate $M(C_6H_8)(C_7H_{10})^+$ and $M(C_7H_{10})_2^+$, respectively (reactions 43 and 44). No methane loss is observed in either reaction.

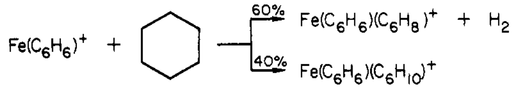

(43)


(44)

A plot of CID product ion abundances vs. kinetic energy for $Co(C_6H_8)(C_7H_{10})^+$ is shown in Figure 5. Formation of $Co(C_7H_8)^+$ dominates over $CoC_6H_6^+$ at all the kinetic energies studied. Similar results were obtained for $Fe(C_6H_8)(C_7H_{10})^+$. CID of the product of reaction 44 yields formation of $M(C_7H_8)^+$ and M^+ as the only fragments. Displacement reactions of $Co(C_6H_8)(C_7H_{10})^+$ with acetonitrile yield formation of $Co(C_7H_8)(CH_3CN)^+$ and $Co(C_6H_6)(CH_3CN)^+$ (reactions 45 and 46). $FeC_6H_6^+$ reacts with cyclohexene to produce $Fe(C_6H_6)(C_6H_8)^+$ and $Fe(C_6H_6)(C_6H_{10})^+$ (reactions 47 and 48).

$$Co(C_6H_8)(C_7H_{10})^+ + CH_3CN \xrightarrow{80\%} Co(C_7H_8)CH_3CN^+ + C_6H_{10} \quad (45)$$

$$\xrightarrow{20\%} Co(C_6H_6)CH_3CN^+ + C_7H_{12} \quad (46)$$


(47)
(48)

Only the condensation process, reaction 48, is observed for $CoC_6H_6^+$ and $NiC_6H_6^+$.

Binding Energies of Olefins. All three metal ions (Fe^+, Co^+, and Ni^+) fail to dehydrogenate ethane.[7,8a] If this is the result of the overall process 49 being endothermic, then $D°(M^+-C_2H_4) <$ 33 kcal/mol.[22]

$$M^+ + C_2H_6 \rightarrow MC_2H_4^+ + H_2 \quad (49)$$

However, both Co^+ and Ni^+ react with cyclopentane, producing $MC_2H_4^+$ ions, reaction 20, which requires $D°(M^+-C_2H_4)$ to exceed 36 kcal/mol.[22] Beauchamp et al. have previously concluded that $D°(Co^+-C_2H_4) = 37 \pm 2$ kcal/mol.[12] We also believe that the bond energy of ethene to Ni^+ cannot exceed 36 kcal/mol by much and assign $D°(Ni^+-C_2H_4) = 37 \pm 2$ kcal/mol. Fe^+ reacts with cyclopentane, generating nearly exclusively (99%) dehydrogenation products with only a trace (1%) of $FeC_3H_6^+$ formation (reaction 19). The low abundance of C-C bond cleavage products for reactions of Fe^+ with cyclopentane may be due to the overall processes being endothermic or near thermoneutral. Observation of reaction 19 for Fe^+ implies $D°(Fe^+-C_3H_6) > 36$ kcal/mol. It appears that this value is a reliable lower limit to the $Fe^+-C_3H_6$ binding energy. Complete absence of $FeC_3H_6^+$ formation from reaction with cyclohexane implies $D°(Fe^+-C_3H_6) < 39$ kcal/mol.[22] Therefore, $D°(Fe^+-C_3H_6)$ is assigned the value 37 ± 2 kcal/mol. Both Co^+ and Ni^+ react with cyclohexane, generating $MC_3H_6^+$ ions, indicating that $D°(Co^+-C_3H_6)$ and $D°(Ni^+-C_3H_6)$ exceed 39 kcal/mol.

Larger olefins are bound more strongly to metal ion centers than smaller olefins. This is clearly demonstrated by ligand diaplacement studies,[9,36] reactions with olefins,[9,30] and CID of ethene-propene-metal ion complexes.[9,30] It appears that the binding energy of propene is roughly 3 kcal/mol greater than that for ethene. Hence, $D°(Fe^+-C_2H_4)$ is assigned the value 34 ± 2 kcal/mol. Using photoionization, Distefano reported $D°(Fe^+-CO) = 60.5 \pm 2$ kcal/mol.[38] Recently, Beauchamp[7b] suggested that the threshold for $FeCO^+$ formation appeared closer to 12.40 eV than 11.53 eV as reported by Distefano. This lowers $D°(Fe^+-CO)$ to 37.6 kcal/mol. Further evidence for this lower binding energy for CO is that $FeCO^+$ photodissociates at λ >660 nm, indicating that $D°(Fe^+-CO) < 43$ kcal/mol.[39] In addition, C_2D_4 has been observed to displace CO from $FeCO^+$,[40] indicating that $D°(Fe^+-C_2D_4) > D°(Fe^+-CO)$. Hence, it appears that $D°(Fe^+-CO)$ may not exceed 34 kcal/mol.

Conclusions

In general, dehydrogenation products dominate the reactions of Fe^+, Co^+, and Ni^+ with cyclic alkanes. This is in sharp contrast to reactions with aliphatic alkanes, where C-C bond cleavage

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(38) Distefano, G. *J. Res. Natl. Bur. Stand., Sect A* **1970**, *74A*, 233.

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(40) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808.

products dominate.[6,7,8a,9] All three metal ions react with cyclobutane to produce products in which the ring has been cleaved. Hence, a mechanism involving initial insertion into a C–C bond is postulated (Scheme II). Dehydrogenation products for reactions with cyclopentane and cyclohexane generate complexes that have retained the integrity of the ring. A mechanism involving initial oxidative addition across a C–H bond may be involved; however, this seems unlikely. An alternative mechanism is presented in Scheme VI and involves initial insertion into a C–C bond followed by α-hydride abstraction with concurrent regeneration of the ring. This mechanism requires α-hydride abstraction to be more facile than β-hydride abstraction for metallacyclohexanes and metallacycloheptanes. Ring-cleavage products are also observed for reactions of Co^+ and Ni^+ with cyclopentane and cyclohexane and are proposed to proceed by initial insertion into a C–C bond followed by reversible β-hydride shifts generating a primary alkene–metal ion complex which decomposes according to Scheme IX. Dehydrogenation of deuterated metallacyclopentanes supports this decomposition mechanism.

Several rapid secondary reactions are also observed. A particularly interesting reaction is seen for (ethene)metal(+) which reacts readily with cyclobutane to generate a bis(ethene)–metal ion complex. (Alkene)metal(+) complexes are unreactive with aliphatic alkanes.[29] The bis(ethene)–metal ion complexes are not in equilibrium with metallacyclopentanes as observed in several solution-phase studies.[27] In addition, both Fe^+– and Co^+–cycloalkadiene products react readily with their corresponding cyclic alkanes via multiple dehydrogenations. Similar behavior has been observed for reactions of Fe^+– and Co^+–alkadiene complexes with aliphatic alkanes.[29] In a related study, (cyclopentadienyl)nickel(+) reacts with cyclic alkanes via dehydrogenations.[14] Six sequential H/D exchanges were observed for both $Co\text{-}c\text{-}C_5H_6^+$ and $Fe\text{-}c\text{-}C_5H_6^+$ species with D_2. Reactions of the monodeuterated $M\text{-}c\text{-}C_5H_5D^+$ ions with cyclopentane indicated that the hydrido–cyclopentadienyl complex, **20**, is the reactive species for Fe^+ while the cyclopentadiene species is the reactive form for Co^+.

Acknowledgement is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (Contract DE-AC02-80ER10689) for supporting this research and to the National Science Foundation (Grant CHE-8002685) for providing funds for the purchase of the FTMS. We also gratefully thank Marc Wise, Chemistry department, Purdue University, for construction of the 5.2-cm cubic trapping cell.

Registry No. Fe^+, 14067-02-8; Co^+, 16610-75-6; Ni^+, 14903-34-5; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclopentene, 142-29-0; cyclohexane, 110-82-7; cyclohexene, 110-83-8; methylcyclohexane, 108-87-2.

Ab Initio Calculation of Resonance Energies. Benzene and Cyclobutadiene

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Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235. *Received April 25, 1983*

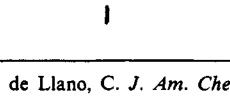
Abstract: Optimum geometries and energies of the all-trans linear polyenes butadiene and hexatriene are obtained with a 6-31G* basis and those of butadiene to pentadecaene in a 3-21G basis. As in semiempirical methods, the energy is a very nearly linear function of chain length. This allows the construction of a Dewar-type aromaticity reference and the computation of ab initio resonance energies for benzene and cyclobutadiene.

It had become apparent by the 1950's that there is very little correlation of the observed stability and chemical behavior of cyclic conjugated systems with Hückel delocalization energy (DE). As more sophisticated theoretical techniques became available, they were also used to compute DE, although with little improvement over the Hückel results. However, in 1969 Dewar and de Llano published resonance energies calculated by the Pariser–Parr–Pople (PPP) method that gave a significant improvement in agreement between theory and experiment.[1] At first sight this success appears to be due to the improved method of computing π energy, but the authors also made a second and more significant change. The Hückel DE of a conjugated hydrocarbon with a Kekulé structure containing n double bonds is defined as the difference between the π energy of the molecule and that of n ethylene units. Dewar and de Llano replaced this ethylene reference by another.

Their new reference structure was based on an earlier observation by Dewar and Gleicher that the acyclic linear polyenes (**1**) are additive in energy.[2] That is, a plot of the calculated π energies of the series **1** vs. n gives an extremely good straight line. This is equivalent to saying that in a linear polyene with $(n + 1)$ single bonds and $(n + 2)$ double bonds, single and double bond energy terms $E^{\pi}_{\mathrm{C-C}}$ and $E^{\pi}_{\mathrm{C=C}}$ can be determined such that the π energy of the polyene is accurately given by

$$E_\pi \approx (n + 1)E^{\pi}_{\mathrm{C-C}} + (n + 2)E^{\pi}_{\mathrm{C=C}} \qquad (1)$$

Dewar and de Llano demonstrated that in the PPP approximation a similar additivity also holds for all acyclic conjugated polyenes. On the other hand, for a cyclic molecule this bond energy sum does not always approximate the actual π energy. The bond energy sum is defined as the reference energy, and the difference between this reference energy and the actual energy of the cyclic system is defined as resonance energy (RE). It represents the additional (aromatic), lack of (nonaromatic), or decreased (antiaromatic) stability of the particular cyclic system relative to the additive reference structure. For example, the RE of benzene is the difference between the computed energy of benzene and that of the reference structure which can be thought of as the hypothetical molecule cyclohexatriene (eq 2). Note that the reference



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(1) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789.

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