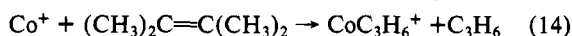
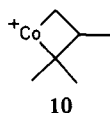


The apparent endothermicity of reaction 14 poses another

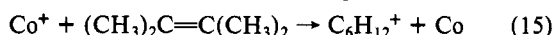


interesting question since the metallacycle 10, presumably can



be formed as in Scheme II and should be able to cleave to eventually eliminate propene.¹⁰ It is possible that the quaternary carbon influences the stability of the various metallacyclobutanes possible in this system such that only certain cleavages and/or isomerizations are likely.

Unique among the reactions of Co^+ with hydrocarbons in this and other studies^{2,3,6} is the observation of process 15, a charge-



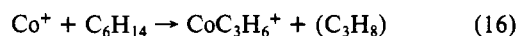
transfer reaction. At higher energies, this product is the major one observed (55% at a relative kinetic energy of 3.5 eV). As noted previously, with the surface ionization source at 2500 K, up to 19% of Co^+ ions may be in the ^5F excited state manifold at 0.42 eV, which is very close to the 0.44-eV endothermicity of reaction 15.²⁴ Near-resonant charge transfer from this component of the Co^+ beam may remain important at high energies.

Conclusion

Results of this study are in good agreement with that of I. In

(24) This is the difference between the ionization potential of 2,3-dimethyl-2-butene (8.30 ± 0.02 eV: Bralsford, R.; Harris, P. V.; Price, W. C. *Proc. R. Soc. London, Ser. A* 1960, 258, 459), and that of cobalt (7.86 ± 0.02 eV: Moore, C. E. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Std.)* 1970, NSRDS-NBS 34).

all cases where secondary reactions of cobalt ion-alkene complexes are believed to occur in I, the same process is observed in the direct reaction of Co^+ with the alkene. Indeed, several reactions which did not fit the general mechanism outlined in I are accounted for by secondary reactions of alkene complexes. An example is process 16, where the hexane isomers are 3-methylpentane and 2,2-di-



methylbutane. These reactions, not explained in I, can occur via initial formation of CH_4 and $\text{CoC}_5\text{H}_{10}^+$. The ionic product undergoes further reaction by cleaving to yield C_2H_4 and CoC_3H_6^+ .

The present study also provides additional evidence that the initial step of the reaction of Co^+ with hydrocarbons is oxidative addition of a carbon-carbon or carbon-hydrogen bond to the metal. In the case of the alkenes, the double bond directs this addition to allylic bonds. Presuming that the Co^+ -allyl binding energy exceeds a comparable Co^+ -alkyl bond, as seems likely, this initial step is thermodynamically more favorable for the alkenes than for the alkanes. Subsequent abstraction of a β -hydrogen and reductive elimination completes the mechanism which accounts for the major products in all systems examined. This mechanism also explains why product distributions are strongly dependent on the carbon skeleton, as in I, but not on location of the double bond.

The cleavage reactions of the butenes and the branched pentenes and hexenes are not easily explained. The proposed intermediacy of a metallacyclobutane species seems reasonable in light of related solution-phase studies and the ease with which β -H transfer to and from Co^+ takes place.^{2,22} However, alternate mechanisms could explain these results. Labeling studies would help to substantiate the proposed mechanisms.

Acknowledgment. This research was supported in part by the United States Department of Energy.

Ion-Beam Studies of the Reactions of Atomic Cobalt Ions with Cycloalkanes in the Gas Phase. Formation and Decomposition of Chemically Activated Metallacycles

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Contribution No. 6312 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. Received January 21, 1981

Abstract: An ion-beam apparatus is employed to study the reaction of singly charged cobalt positive ions with cyclopropane, cyclobutane, cyclopentane, and cyclohexane. In all cases, ring cleavage reactions are observed. These processes find analogy with the decompositions of solution-phase metallacycles by C-C bond cleavage. In all systems but cyclopropane, dehydrogenation of the cycloalkane is also observed. Multiple dehydrogenation occurs with cyclopentane [yielding $\text{Co}(\text{C}_5\text{H}_6)^+$] and cyclohexane [yielding $\text{Co}(\text{C}_6\text{H}_8)^+$ and $\text{Co}(\text{C}_6\text{H}_6)^+$]. The present results are contrasted with the reactions of Co^+ with the isomeric alkenes.

The importance of metallacyclic species as catalytic intermediates has prompted numerous recent studies.²⁻¹¹ However, none¹²

have been conducted in the gas phase where the reactivity and stability of such intermediates may be studied in the absence of solvent interactions and ligand effects.¹³ Recent studies^{14,15} in

- (1) To whom correspondence should be addressed.
- (2) Stone, F. G. A. *Pure Appl. Chem.* 1972, 30, 551.
- (3) (a) Grubbs, R. H. *Prog. Inorg. Chem.* 1978, 24, 1. (b) Grubbs, R. H.; Miyashita, A. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, p 151.
- (4) (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* 1976, 98, 6521. (b) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *Ibid.* 1976, 98, 6529.
- (5) Ephritikhine, M.; Green, M. L. H.; MacKenzie, R. E. *J. Chem. Soc., Chem. Commun.* 1976, 619.
- (6) (a) Perkins, D. C. L.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.* 1978, 154, C16. (b) Al-Essa, R. J.; Puddephatt, R. J.; Tipper, C. F. H.; Thompson, P. J. *Ibid.* 1978, 157, C40. (c) Al-Essa, R. J.; Puddephatt, R. J.; Quyyer, M. A.; Tipper, C. F. H. *J. Am. Chem. Soc.* 1979, 101, 364.

- (7) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* 1977, 139, 157.
- (8) Cushman, B. M.; Brown, D. B. *J. Organomet. Chem.* 1978, 152, C42.
- (9) (a) Johnson, T. H. *J. Org. Chem.* 1979, 44, 1356. (b) Johnson, T. H.; Cheng, S. *J. Am. Chem. Soc.* 1979, 101, 5277.
- (10) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. *J. Am. Chem. Soc.* 1979, 101, 4234.
- (11) Stockis, A.; Hoffman, R. *J. Am. Chem. Soc.* 1980, 102, 2952.
- (12) Metallacyclic intermediates are postulated in two previous studies concerning gas-phase metal carbenes: (a) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* 1981, 74, 2819. (b) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1979, 101, 6449.
- (13) The importance of such effects has been amply illustrated. See, in particular, ref 3, 4, and 6.

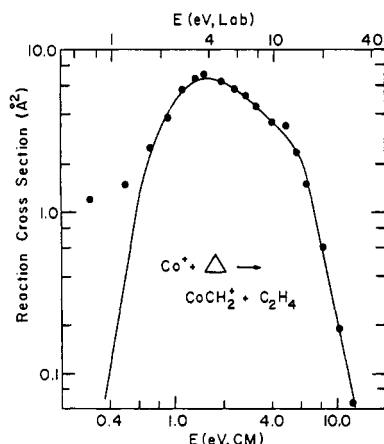


Figure 1. Variation in experimental cross section with relative kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale) for reaction of Co^+ with cyclopropane to yield CoCH_2^+ . The curve is a fit to the data by using a model proposed previously. Both the fit and the model are detailed in ref 12a.

Table I. Product Distributions for Reactions of Co^+ with Cyclic Alkanes Measured at ~ 1 -eV Relative Kinetic Energy

cyclic alkane	neutral products			
	$n\text{H}_2$	CH_4	C_2H_4	C_3H_6
C_3H_6			1.0 ^a	
C_4H_8	0.86		0.14	
C_5H_{10}	0.44	0.03	0.45	0.08
C_6H_{12}	0.76	0.03	0.03	0.18

^a Variation of reaction cross section with ion energy indicates an endothermic process.

our laboratories have demonstrated that the initial step in the reaction of cobalt ions with hydrocarbons is oxidative addition of a carbon-carbon or carbon-hydrogen bond to the metal center. Thus, interaction of Co^+ with cyclic alkanes might be expected to produce metallacycles. While these intermediates can not be detected directly, characteristic decomposition reactions can be observed.

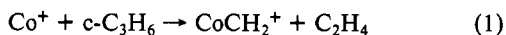
In the present study, an ion-beam apparatus is used to examine the reactions of cobalt ions with cyclopropane, cyclobutane, cyclopentane, and cyclohexane. Both dehydrogenation and ring cleavage products are observed. The former are generally characteristic of initial C-H bond addition. The latter are shown to be analogous with the products of solution-phase metallacycles which decompose by C-C bond cleavage.

Experimental Section

The ion-beam apparatus and experimental techniques have been detailed elsewhere.^{12a,14,15} A brief description appropriate for the present work is given in the experimental section of our related study of Co^+ with alkenes.¹⁵

Results and Discussion

Reaction of Co^+ with Cyclopropane. The major product observed upon interaction of cobalt ions with cyclopropane is the cobalt carbene ion, reaction 1. The cross section for this process,



shown in Figure 1, decreases with decreasing energy below 1.5 eV in the center of mass, suggesting an endothermic reaction. A detailed analysis of this and related results, reported previously,^{12a} yielded the cobalt-carbene ion bond energy, $D^0(\text{Co}^+-\text{CH}_2) = 85 \pm 7$ kcal/mol. Other products observed in this system include C_3H_5^+ , CoC_2H_2^+ , CoC_2H_4^+ , and CoC_3H_4^+ . All are formed in

Scheme I

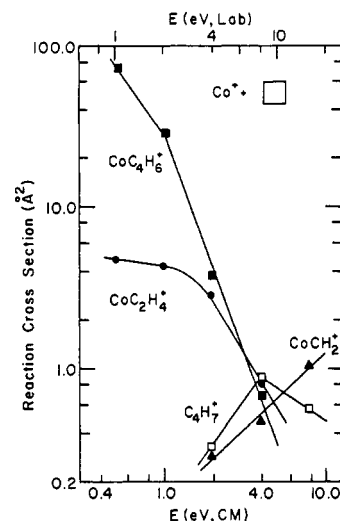
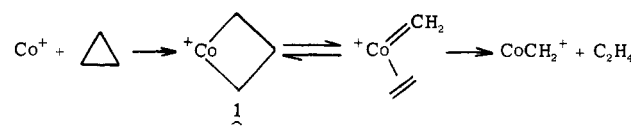


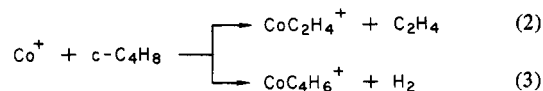
Figure 2. Variation in experimental cross section with relative kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale) for the interaction of Co^+ with cyclobutane.

highly endothermic reactions and cumulatively account for less than 10% of the product yield at all energies. The collisionally stabilized CoC_3H_6^+ adduct is also observed.

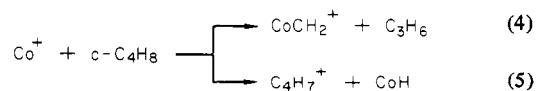
Reaction 1 is postulated to occur via a metallacyclobutane intermediate 1 as in Scheme I. The various reaction steps are well-known for the formation and decomposition of solution-phase metallacyclobutanes.^{3,4,6,9,10} The initial step of Scheme I, oxidative addition of a C-C bond to Co^+ , has been shown to occur for the reactions of cobalt ions with acyclic alkanes.¹⁴ It should be noted that reductive elimination of cyclopropane from 1 as well as isomerization to eventually yield Co^+ and propene may be occurring in this system. We have no means to monitor either process in this experiment.

In contrast with the results for larger cyclic alkanes, cyclopropane does not undergo appreciable dehydrogenation upon reaction with Co^+ . This is undoubtedly due to the fact that dehydrogenation to form cyclopropene requires 53 kcal/mol.¹⁶ The binding energy of Co^+ to alkenes is typically about 35–40 kcal/mol,^{14,15} and the reaction is thus substantially endothermic.

Reaction of Co^+ with Cyclobutane. Results for the interaction of cobalt ions with cyclobutane are shown in Figure 2. Cross sections for processes 2 and 3 decrease with increasing energy,



indicating both are exothermic. At higher energies the endothermic reactions 4 and 5 are observed. Other minor products include CoC_2H_2^+ , CoC_3H_5^+ , and several alkyl ions.



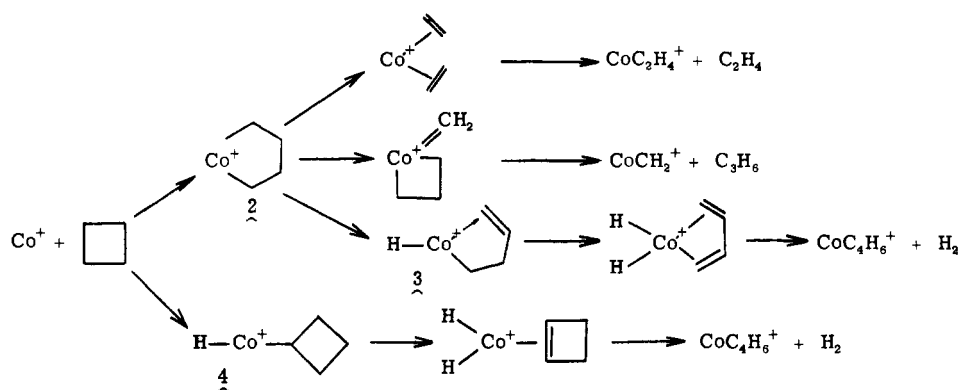
Decomposition of metallacyclopentanes in solution usually proceeds via symmetric ring cleavage to yield the bis(ethene) complex.^{3,4,11} Similarly, reaction 2 may proceed via formation

(14) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784.

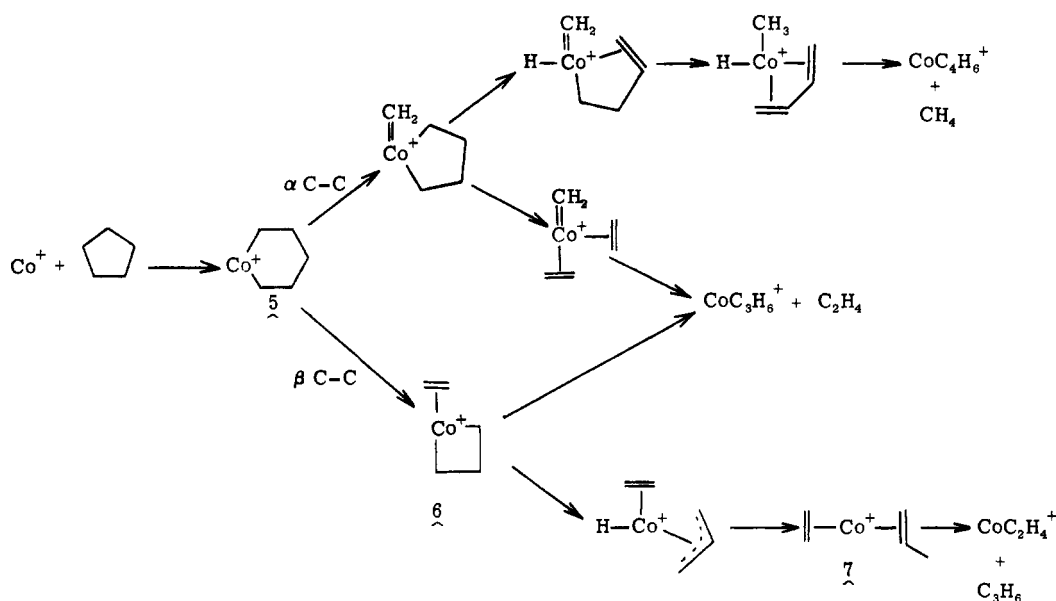
(15) Armentrout, P. B.; Beauchamp, J. L. preceding paper in this issue.

(16) Supplementary thermochemical information concerning hydrocarbons is taken from: Stull, D. R.; Westrum, E. F.; Sinke, G. C. "Chemical Thermodynamics of Organic Compounds", Wiley: New York, 1969.

Scheme II



Scheme III



of the cobaltacyclopentane ion, 2, as suggested in Scheme II. The alternate ring cleavage process, α -C-C cleavage, accounts for reaction 4. With use of the cobalt carbene ion bond energy of 85 ± 7 kcal/mol,^{12a} this reaction is calculated to be endothermic by 6 ± 8 or 14 ± 8 kcal/mol,¹⁶ depending on whether the neutral product is propene or cyclopropane, respectively. The endothermic threshold for the CoCH_2^+ product could not be determined with sufficient accuracy to distinguish these possibilities.

The dehydrogenation reaction, process 3, can conceivably occur by the two pathways shown in Scheme II. Both should be exothermic, and in analogy with the cyclopentane and cyclohexane systems discussed below, both are probably occurring. Observation of C_4H_7^+ at high energies provides no means of distinguishing these pathways since it could result from decomposition of 3 or 4.

Reductive elimination in 2 to return to reactants or in 3 to yield Co^+ and 1-butene may represent significant decomposition pathways for the cobaltacyclopentane ion. However, as in the cyclopropane system, no means of monitoring these reactions exist in the present experiment. This general conclusion will also be valid for the cyclopentane and cyclohexane systems.

Reaction of Co^+ with Cyclopentane. Few solution-phase studies have been performed on metallacyclohexanes.^{3,4} Miyashita and Grubbs^{3,17} have reported that nickelacyclohexane and titanacyclohexanes which decompose by C-C bond cleavage yield predominantly ethene, some methane and butenes and little or no propene. Labeling studies indicated α -C-C cleavage of the ring seemed to occur more often than β -C-C cleavage. Qualitatively,

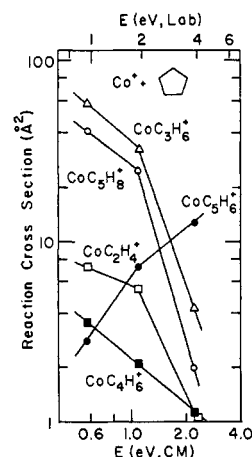
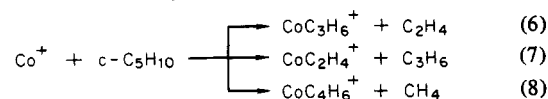


Figure 3. Variation in experimental cross section with relative kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale) for the interaction of Co^+ with cyclopentane.

the results shown in Figure 3 correspond nicely with these observations. Loss of ethene, process 6, is the prevailing ring cleavage



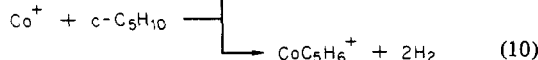
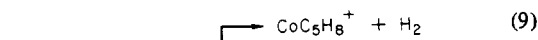
product ($\sim 80\%$ at 1 eV in the center of mass). As indicated in Scheme III, such a reaction can occur either by α - or β -C-C cleavage. Process 7 presumably occurs via β -C-C cleavage but

(17) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7418.

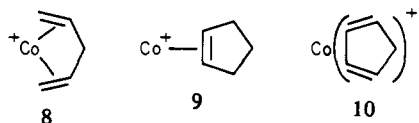
requires rearrangement of **6** to the bis(olefin) complex **7** for reasons discussed below. Observation of reaction **7** may indicate that isomerization of cobaltacyclobutane ions to a propene complex is a major reaction pathway. Loss of methane, process **8**, must be the result of α cleavage of **5**, Scheme III. As postulated above for the cobaltacyclopentane ion, Scheme II, sequential β -hydrogen abstraction and reductive elimination yield the cobalt ion-butadiene complex.

Observation that reactions **6** and **7** are exothermic implies that the binding energies of ethene and propene to Co^+ exceed 36 kcal/mol, the energy necessary to convert cyclopentane to these olefins.¹⁶ A previous study had concluded $D^0(\text{Co}^+-\text{C}_2\text{H}_4) < 33$ kcal/mol.¹⁴ The lower limit of 36 kcal/mol is the more reliable value, but it seems likely that the binding energy of C_2H_4 to Co^+ cannot exceed this limit greatly. We conclude that $D^0(\text{Co}^+-\text{C}_2\text{H}_4) = 37 \pm 2$ kcal/mol. This discussion also serves to discount the possibility that the neutral product of reaction **7** is cyclopropane, formed by reductive elimination in **6**, since this process would require an additional 8 kcal/mol.¹⁶

Dehydrogenation, process **9**, may occur by two pathways,



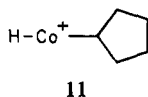
analogous to Scheme II. Either the (1,4-pentadiene)cobalt ion complex **8** or the (cyclopentene)cobalt ion complex, **9**, is produced.



The double dehydrogenation, process **10**, is most easily explained by sequential β -hydrogen abstraction from **9** and reductive elimination of H_2 , yielding the (cyclopentadiene)cobalt ion complex **10**. This product is not observed in the reactions of Co^+ with the acyclic C_5H_{10} isomers.¹⁵ This suggests that the integrity of the C_5 ring is maintained for the CoC_5H_6^+ product and probably the CoC_5H_8^+ product.

The exothermicity and endothermicity of reactions **9** and **10**, respectively, imply that $D^0(\text{Co}^+-\text{c-C}_5\text{H}_8) > 26$ kcal/mol and $D^0(\text{Co}^+-\text{c-C}_5\text{H}_6) < 50$ kcal/mol.¹⁶ These values are in accord with binding energies of acyclic alkenes and alkadienes determined in previous studies.^{14,15}

At higher energies the alkyl ion C_5H_9^+ is observed. Such a species may be formed by breaking the cobalt-carbon bond in the intermediate **11** proposed to explain reaction **9**. Observation



of C_5H_9^+ and not CoH^+ in this system is taken to indicate that $\text{IP}(\text{CoH}) > \text{IP}(\text{c-C}_5\text{H}_9)^{18} = 7.21$ eV.¹⁹

Reaction of Co^+ with Cyclohexane. No solution-phase studies concerning decomposition of metallacycloheptanes via C-C cleavage have been reported.²⁰ Results for the interaction of cobalt ions with cyclohexane are shown in Figure 4. Processes **11**–**14**,

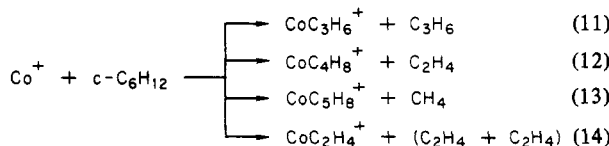


Figure 4a, seem typical of C-C cleavage reactions of metallacycles

(18) This conclusion was reported earlier¹⁴ and agrees with limits placed on $\text{IP}(\text{CoH})$ after examination of many systems.

(19) (a) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067. (b) Houle, F. A. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1979.

(20) The only published study⁴ concerning metallacycloheptanes reported decomposition to yield 1- and 2-hexenes exclusively.

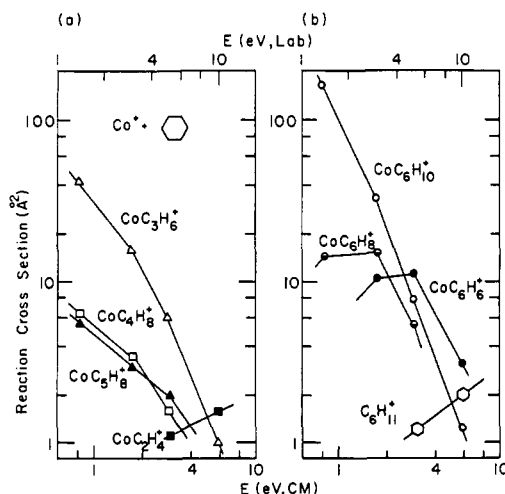


Figure 4. Variation in experimental cross section with relative kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale) for the interaction of Co^+ with cyclohexane yielding (a) ring cleavage products and (b) dehydrogenation products.

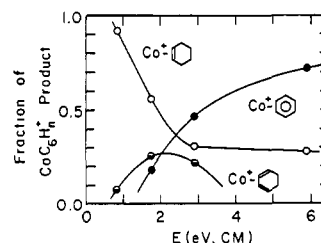
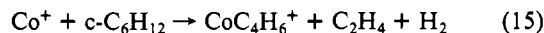
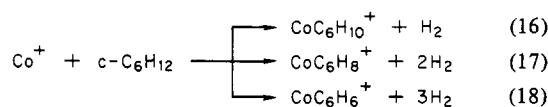


Figure 5. Variation in product distribution with relative kinetic energy in the center of mass for the three dehydrogenation products resulting from interaction of Co^+ with cyclohexane (reactions **16**–**18**). The sequential nature of the dehydrogenation process is evident.

and would appear to involve α - β -, and γ -C-C cleavages. The exothermicity of reactions **11** and **12** provides a lower limit of 39 kcal/mol for the binding energies of propene and butene, respectively, to cobalt ions. The endothermicity of reaction **14** may imply $D^0(\text{Co}^+-\text{C}_2\text{H}_4) < 39$ kcal/mol¹⁶ and suggests the neutral products indicated. At higher energies, CoC_4H_6^+ is also observed. The endothermic behavior associated with formation of this product suggests that it is formed in process **15** and is a secondary reaction of a CoC_4H_8^+ product.



The predominant reactions of cobalt ions with cyclohexane are the dehydrogenation processes **16**–**18**, Figure 4b. Mechanistic



considerations are analogous to the cyclopentane system. As suggested for that system, the hydrocarbon ring probably remains intact in these products. At higher energies, the $\text{C}_6\text{H}_{11}^+$ ion is observed. CoH^+ is also observed but in much lower yields. This is taken to indicate that $\text{IP}(\text{CoH}) > \text{IP}(\text{c-C}_6\text{H}_{11})^{18} = 7.15$ eV.¹⁹

The enthalpy change associated with removal of the first, second, and third molecules of hydrogen from cyclohexane are 28, 27, and -6 kcal/mol, respectively.¹⁶ Thus the exothermicity of reaction **16** implies that $D^0(\text{Co}^+-\text{c-C}_6\text{H}_{10}) > 28$ kcal/mol. Since H_2 may carry off part of the excess energy, it is not possible to characterize the energetics of the remaining steps in the sequence. The stepwise nature of the dehydrogenation processes is emphasized by the product distribution shown for these reactions alone in Figure 5.

Comparison with Alkene Systems. Many of the products observed when Co^+ reacts with cycloalkanes are also observed with

the isomeric alkenes as the neutral reactants.¹⁵ However, product distributions and the behavior of cross sections with kinetic energy distinguish the cyclic from the acyclic systems. Most striking are the differences in reactivity of cyclopropane and propene (for which no reactions were detected at low energies) and the multiple dehydrogenation of cyclopentane, reaction 10, and cyclohexane, reactions 17 and 18, a process not observed for any pentene or hexene isomer. Interestingly, Allison and Ridge²¹ have observed such multiple dehydrogenations in the reactions of Ti^+ and TiCl^+ with alkenes. They speculate that dehydrocyclization reactions result in the production of metal ion-cyclic alkene complexes. No carbon-carbon bond cleavage reactions were observed in those studies in contrast to the present results.

Conclusion

While the case for the intermediacy of cobaltacycle ions in the reactions of Co^+ with cyclic alkanes is equivocal, the observations made in the present study are consistent with such a mechanism. Unfortunately, no conclusions can be drawn concerning the relative rates of metallacycle decomposition via ring cleavage processes vs. reductive elimination reactions yielding the reactant cyclic alkane or an isomerized alkene. The present results do suggest, however, that of the ring cleavage reactions, symmetric or nearly symmetric C-C bond cleavage is preferred. Cleavage at all positions does occur, however.

(21) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* 1977, 99, 35.

As in previous studies,^{14,15} the structure of the reactant hydrocarbon is an important factor determining product distributions. Thus, reactions of the cyclic alkanes differ appreciably from those of the isomeric alkenes. Since the product ions CoC_3H_6^+ , CoC_4H_8^+ , and $\text{CoC}_6\text{H}_{10}^+$ are observed in the cyclopentane and cyclohexane systems but not in acyclic alkene¹⁵ or alkane¹⁴ systems, dehydrocyclization of the latter hydrocarbons is regarded as improbable.

In studies related to the present experiments, reactions of CpNi^+ ions, where $\text{Cp} \equiv (\eta^5\text{-C}_5\text{H}_5)$, with cyclic alkanes have been examined.^{22,23} While no cleavage reactions occur, dehydrogenation of cyclobutane and multiple dehydrogenations of cyclopentane and cyclohexane, all exothermic, are observed. In another study,²⁴ the product ions $\text{CpCo}(\text{C}_6\text{H}_{10})^+$, $\text{CpCo}(\text{C}_6\text{H}_8)^+$, and $\text{CpCo}(\text{C}_6\text{H}_6)^+$ were observed in an ionized mixture of $\text{CpCo}(\text{CO})_2$ and cyclohexane. From a comparison of these results with the present study it is apparent that the cyclopentadienyl ligand can greatly affect the chemistry of the metal center. Specifically, the processes initiated by insertion into a C-C bond are not observed.

Acknowledgment. This work was supported in part by the United States Department of Energy.

(22) (a) Corderman, R. R. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 1977. (b) Corderman, R. R.; Beauchamp, J. L., submitted for publication in *J. Organomet. Chem.*

(23) Müller, J.; Goll, W. *Chem. Ber.* 1973, 106, 1129.

(24) Müller, J. *Adv. Mass. Spectrom.* 1974, 6B, 823.

Negative Ion States of d^6 Transition-Metal Hexacarbonyls

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Abstract: The energies of the low-lying unstable negative ion states of $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ have been obtained by electron transmission spectroscopy. Calculations employing the SCF $X\alpha$ method indicate that these compounds possess a number of stable negative ion states and that the observed unstable states arise from electron capture into the antibonding ligand field orbitals and other empty orbitals correlating with the 2π and 6σ orbitals of free CO.

The study of the electronic structure of organometallic compounds has enjoyed a renaissance over the past few years. In particular the transition-metal carbonyl complexes have received a good deal of attention. This is not surprising since the CO-metal bond is quite common in organometallic chemistry. Additionally, an understanding of the CO-metal bond is fundamental to the study of CO chemisorption as well as catalytic reactions at metal surfaces.

Ultraviolet photoelectron spectroscopy (UPS), first extensively applied to studies of hydrocarbons, has recently been employed to measure the ionization potentials of organometallics in order to learn about the energies of the occupied valence orbitals of these compounds.² However, a complete picture of the electronic structure requires information on the low-lying unoccupied orbitals. Much of this information is available from electron transmission spectroscopy³ (ETS), the experiment conjugate to UPS. Whereas UPS measures the energy required to remove an electron from an occupied orbital, ETS measures the energy of a negative ion

state arising from electron capture into an unoccupied orbital. A limitation to ETS is that only the energies associated with unstable negative ions are accessible. That is, only negative electron affinities can be determined by ETS. This technique was first applied in studies of atoms and di- and triatomics.⁴ Subsequently, ETS has been applied in investigations of the properties of π^* orbitals of unsaturated hydrocarbons.³ We report here the first extension of the technique to transition-metal complexes.

The transition-metal hexacarbonyls $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ were chosen for their volatility and their simple and symmetrical geometry and because of their d^6 electronic configuration. Simple ligand field theory suggests that the first unoccupied orbital is the antibonding σ molecular orbital of e_g symmetry and that the splitting in the octahedral ligand field is sufficiently large that occupation of this orbital may give rise to an unstable temporary negative ion state. Gray and Beach⁵ point out that a number of antibonding π orbitals, mainly localized on the ligands, can be expected at energies comparable to that of the

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