lated for the EDTA/DFO kinetics, are operative in this region.

In a previous study, Lovenberg et al.[19] found that metal ion transfer from ferric citrate to ferrichrome is relatively rapid ($t_{1/2} \sim 10$ min). This has been interpreted as indicating a generally rapid rate of iron exchange and transfer to and between siderophores. However, citrate is a bidentate ligand which, when present in the concentrations used in the Lovenberg experiment, forms a bis (two to one) complex with Fe(III). The reduced denticity of the citrate ligand and the ease with which its complex partially dissociates to give free coordination sites on the metal are consistent with the relatively rapid exchange observed for this system, but is in marked contrast to the dramatically slower rates observed in this study.

As described in the introduction of this paper, there are three limiting mechanisms of siderophore transport that have been proposed. In transport studies of labeled ferric and chromic complexes of ferrioxamine B by *Salmonella typhimurium*,[24] it was found that neither of the obtained chromic complex isomers was transported into the microbe, and the $^{55}$Fe label was taken up more rapidly than the $^{3}$H ligand label. Mechanism 3 (transport of intact complex and metal release by ligand destruction) does not pertain in this system, since the ferrioxamine B remains intact. Mechanism 2 (the active transport of the intact metal complex) seems unlikely, since neither chromic complex was transported. Only if it is hypothesized that another, not isolated, isomer is *specifically* absorbed can mechanism 2 be operative. This leaves mechanism 1 (involving ligand exchange at the cell surface) as the most likely process in this system, and requires a rapid rate of iron removal from ferrioxamine B in order to be consistent with the rapid uptake of $^{55}$Fe (complete in 30 min) by *S. typhimurium*. Even if mechanism 2 were operative, a rapid mechanism for iron release by ferrioxamine B *inside* the cell is necessary. The results presented here show that the uncatalyzed extraction of iron from ferrioxamine B by EDTA is a relatively slow process (initial rate of $1.4 \times 10^{-10}$ M s$^{-1}$ at pH 7.4 and ~20:1 ratio of EDTA to FeHDFO$^+$)—a rate which is not consonant with the rate of iron uptake in ligand transport experiments. One probable mechanism for the release of iron from trihydroxamates (in addition to the effect of rate enhancement due to high hydrogen ion concentration) is reduction to the ferrous state, which converts the tightly bound ferric complex to the loosely bound ferrous complex, from which the iron can be easily extracted and the intact ligand can be recycled.[26] The feasibility of this mechanism has been established by electrochemical studies of the redox process.[46] An example of this type of metabolic pathway for iron is in the ferrichrome mediated iron transport in *U. sphaerogena*,[47] in which an NADH-dependent ferrichrome reductase (NADH:ferrichrome oxidoreductase) is thought to be active in iron release from this siderophore. Further examples of reductase activity in the catalytic removal of iron from siderophores[48,49] and iron storage proteins[50] can be found in the literature.

In summary, iron release from the trihydroxamate siderophores ferrichrome A and ferrioxamine B is very slow at physiological pH. It is very likely this is generally true for all of the hexadentate siderophores. Since siderophore-mediated iron transport and release is a much more rapid process than the simple exchange kinetics of these Fe(III) complexes, the role of redox reactions in the catalysis of this exchange comes into question. Experiments to elucidate this role are now in progress.

**Acknowledgment.** We wish to thank Drs. C. J. Carrano and W. R. Harris and Mr. V. L. Pecoraro for many helpful discussions. T.P.T. gives special thanks to Ms. M. J. Kappel for assistance with the nonlinear least-squares refinement. This research is supported by the National Institutes of Health through Grant No. AI 11744.

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(46) Cooper, S. R.; McArdle, J. V.; Raymond, K. N. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 3551.

(47) Straka, J. G.; Emery, T. *Biochim. Biophys. Acta* **1979**, *569*, 277.

(48) Brown, K. A.; Ratledge, C. *FEBS Lett.* **1975**, *53*, 262.

(49) Ernst, J. F.; Winkelmann, G. *Biochim. Biophys. Acta* **1977**, *500*, 27.

(50) Sirivech, S.; Driskell, J.; Frieden, E. *J. Nutr.* **1977**, *107*, 739.

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# Ion-Beam Studies of the Reactions of Atomic Cobalt Ions with Alkenes

**P. B. Armentrout, L. F. Halle, and J. L. Beauchamp*[1]**

*Contribution No. 6311 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 reactions of singly charged cobalt positive ions with 12 alkenes. While ethene and propene undergo no exothermic reactons, two processes are observed for larger olefins. One reaction yields cobalt ion alkadiene complexes and either methane or $H_2$. The second process involves cleavage of the alkene into two smaller olefins, one of which remains bound to Co$^+$. A mechanism involving oxidative addition of an allylic C–C or C–H bond to the metal as the initial step is proposed to account for all observed products. Subsequent formation of a cobaltacyclobutane species is postulated for several of the cleavage reactions.

In a recent article (hereafter referred to as I),[2] the reactions of Co$^+$ with saturated hydrocarbons were reported. Exothermic reactions were observed to yield cobalt ion–alkene complexes, and in some systems, small amounts of cobalt ion–alkadiene complexes. At higher collision energies, these latter products often predominated. It was postulated that the alkadiene complexes resulted from subsequent reactions of the initially formed alkene complexes. A simplified potential energy surface for one such system is shown in Figure 1. It demonstrates how the alkene complex intermediate can also be accessed by direct reaction of the alkene with cobalt ions. An examination of such reactions would provide a test of the hypothesis made in I as well as extend the study of the general reactivity of Co$^+$ with hydrocarbons.

Using an ion-beam apparatus, the reactions of Co$^+$ with 12 alkenes have been studied in the present work. It is found that these reactions do indeed yield cobalt ion alkadiene complexes. In addition, cleavage of the alkene into smaller alkenes, one of which remains bound to Co$^+$, is also observed. These unexpected cleavage reactions provide an explanation for several products reported in I which appeared anomalous. A mechanism involving initial formation of an allyl complex is shown to account for all products observed. For some reactions, subsequent conversion

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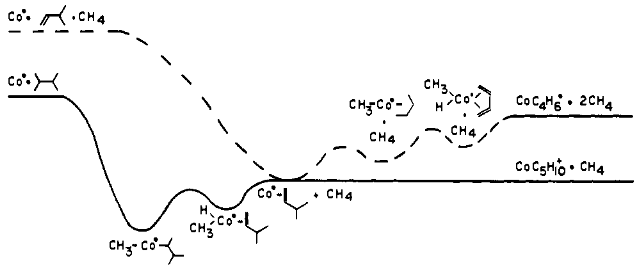

**Figure 1.** Schematic representation of the energy changes involved in the interaction of cobalt ions with 2,3-dimethylbutane (full line) and 3-methyl-1-butene (dashed line).

to a metallacyclobutane intermediate is proposed.

## Experimental Section

The ion-beam apparatus and experimental techniques have been detailed elsewhere.[2,3] In brief, cobalt ions formed by surface ionization primarily in the ground electronic state are mass and energy selected. This ion beam is focussed into a collision chamber containing the reactant gas. Pressures are measured using a capacitance manometer and are maintained such that reactions are the result of a single bimolecular collision. Product ions are extracted from the collision chamber, mass analyzed by using a quadrupole mass filter, and detected by a Channeltron electron multipler operated in a pulse counting mode. Ion signal intensities are corrected for the mass discrimination of the quadrupole mass filter. Neutral products are not detected but can usually be inferred without ambiguity.

Reaction cross sections for specific products, $\sigma_i$, are obtained by using eq 1 and 2 which relate the total reaction cross section, $\sigma$, the number

$$I_0 = (I_0 + \sum I_i)\exp(-n\sigma l) \qquad (1)$$

$$\sigma_i = \sigma I_i / \sum I_i \qquad (2)$$

density of the target gas, $n$, and the length of the collision chamber, $l$ (5 mm), to the transmitted reactant ion beam intensity, $I_0$, and the product ion intensities, $I_i$. It was found with the heavier hydrocarbons that total cross sections were not accurately reproducible. We attribute this effect to substantial loss of elastically scattered $Co^+$ from the reactant beam. Relative cross sections of products (branching ratios) are reproducible, however.

Chemicals were obtained from commercial sources and used as received except for degassing by several freeze–pump–thaw cycles. Samples are at least 99% pure in all cases but 2-pentene which is a mixture of the cis and trans isomers.

## Results and Discussion

**Reaction of Co⁺ with Ethene and Propene.** Results of the interaction of cobalt ions with ethene have been detailed elsewhere.[3] There is no evidence for exothermic reactions; however, reactions 3 and 4, both endothermic, are observed. Interpretation

$$Co^+ + C_2H_4 \longrightarrow \begin{cases} CoH^+ + C_2H_3 & (3) \\ CoCH_2^+ + CH_2 & (4) \end{cases}$$

of the thresholds for these processes yield a cobalt ion–hydride bond energy of 2.3 ± 0.4 eV[3,4] and a cobalt ion–carbene bond energy of 3.7 ± 0.3 eV.[3]

No exothermic reactions of $Co^+$ with propene are observed. Endothermic reactions were not examined.

**Reaction of Co⁺ with Butenes.** The primary reaction of cobalt ions with butenes is dehydrogenation, process 5. The cleavage

$$Co^+ + C_4H_8 \longrightarrow \begin{cases} CoC_4H_6^+ + H_2 & (5) \\ CoC_2H_4^+ + C_2H_4 & (6) \end{cases}$$

reaction 6 is also observed. Results for the four butenes are compared in Figure 2. Cross sections which decrease with increasing energy indicate exothermic reactions. Thus, reactions 5 and 6 are shown to be exothermic for all isomers.[5] Within experimental error, the behavior of the three linear butene systems is identical and differs markedly from the 2-methylpropene system. Not only is the cross section for reaction 5 lower while that for reaction 6 is higher but also reaction 7 is observed in the case of

$$Co^+ + i\text{-}C_4H_8 \rightarrow CoC_3H_4^+ + CH_4 \qquad (7)$$

2-methylpropene. Also the apparent cross section for formation of the adduct $CoC_4H_8^+$ (not shown in Figure 2) is higher in this system than in those of the linear butenes. The adduct is a collisionally stabilized complex as verified by measurements at several pressures.

The equivalent reactivity of the linear butenes suggests that interaction with $Co^+$ induces facile isomerization to yield a common intermediate. In analogy with solution-phase results,[8-11] such

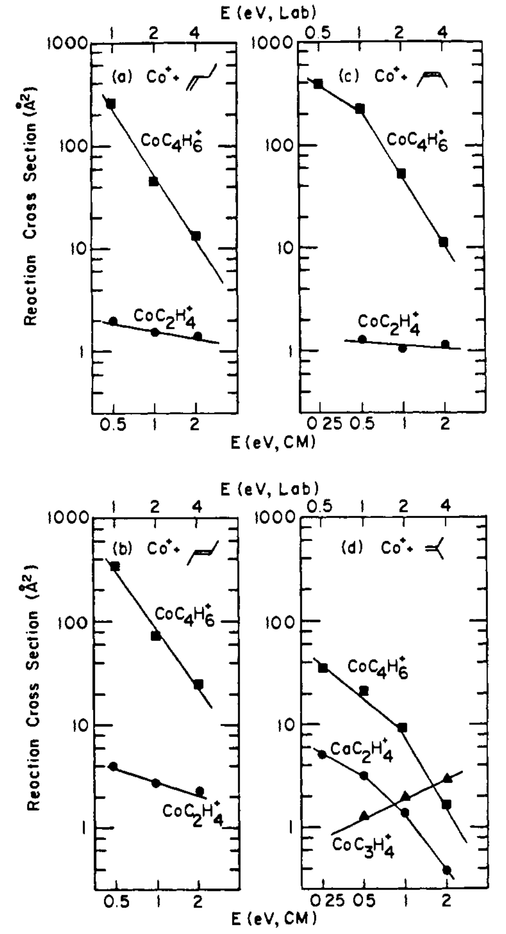

**Figure 2.** Variation in experimental cross section for the reactions of $Co^+$ with (a) 1-butene, (b) 2-*trans*-butene, (c) 2-*cis*-butene, and (d) 2-methylpropene as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale).

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[1] To whom correspondence should be addressed.

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

[3] Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819.

[4] This value differs from that given in ref 3 (>2.2 ± 0.9 eV). The present figure has been recalculated by using the recently published bond dissociation energy, $D_{298}^0$ ($H-C_2H_3$) = 111.1 ± 2.2 kcal/mol. DeFrees, D. J.; McIver, R. T.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334.

[5] The binding energy of 1,3-alkadienes to $Co^+$ would appear to be about 45–60 kcal/mol,[2] that of ethene about 37 kcal/mol,[6] and that of propene and butene >39 kcal/mol.[6] On the basis of these values,[7] all reactions observed to be exothermic in this study are expected to be so.

[6] Armentrout, P. B.; Beauchamp, J. L. following paper in this issue.

[7] 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.

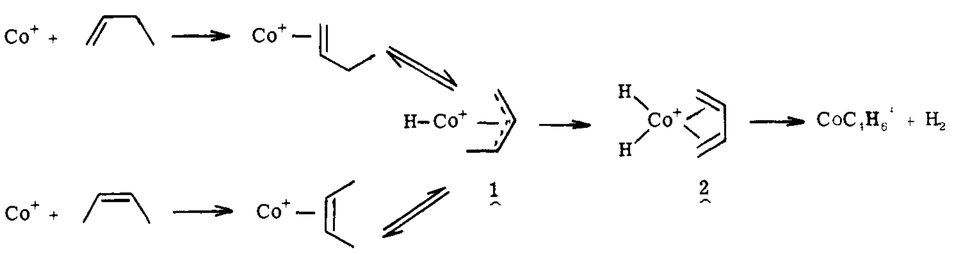
[8] Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 736.

[9] Byrne, J. W.; Blaser, H. U.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3871.

[10] Ephritikhine, M.; Green, M. L. H.; MacKenzie, R. E. *J. Chem. Soc., Chem. Commun.* **1976**, 619.

[11] Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201 and references therein.

Scheme I



Scheme II

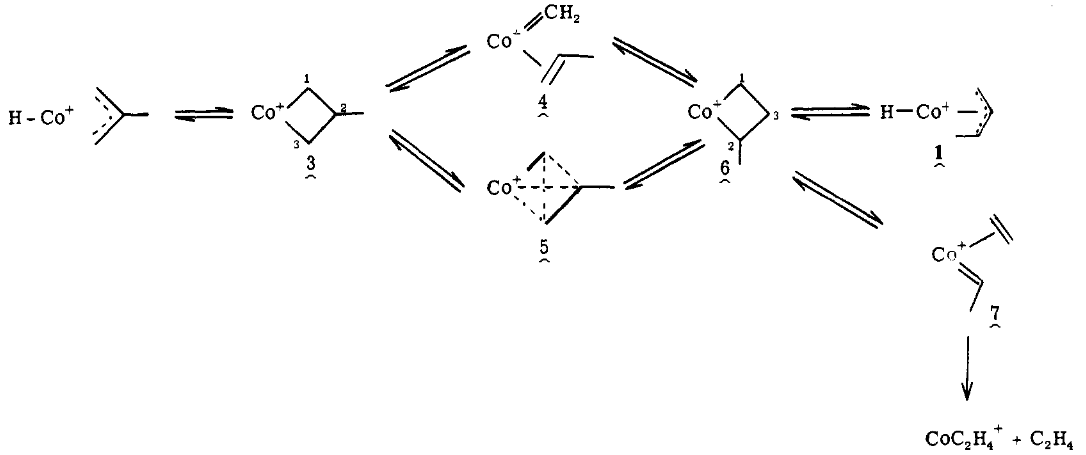


Table I. Product Distributions for Reactions of $Co^+$ with Alkenes Measured at ~1-eV Relative Kinetic Energy[a]

| alkene | isomer | neutral products corresponding to Co(alkadiene)$^+$ products | | | neutral products corresponding to Co(alkene)$^+$ products | | | charge transfer |
|---|---|---|---|---|---|---|---|---|
| | | $H_2$ | $CH_4$ | $(H_2 + C_2H_4)$ | $C_2H_4$ | $C_3H_6$ | $C_4H_8$ | |
| $C_4H_8$ | 1-butene<br>*trans*-2-butene<br>*cis*-2-butene | 0.97 | | | 0.03 | | | |
| | 2-methylpropene | 0.76 | 0.14* | | 0.10 | | | |
| $C_5H_{10}$ | 1-pentene | 0.11 | 0.13 | | 0.58 | 0.18 | | |
| | 2-pentene[b] | 0.28 | 0.33 | | 0.29 | 0.10 | | |
| | 2-methyl-1-butene | 0.46 | 0.26 | | 0.20 | 0.08 | | |
| | 2-methyl-2-butene | 0.34 | 0.30 | | 0.26 | 0.10 | | |
| | 3-methyl-1-butene | 0.35 | 0.35 | | 0.22 | 0.08 | | |
| $C_6H_{12}$ | 1-hexene | 0.05 | 0.01* | 0.06* | 0.15 | 0.64 | 0.09 | |
| | 2,3-dimethyl-2-butene | 0.23 | 0.37 | 0.04* | 0.16 | 0.02* | 0.04 | 0.14* |

[a] Starred products appear to be formed in endothermic processes. All others are produced in exothermic reactions. [b] Mixture of cis and trans isomers.

a process is proposed to occur via formation of an allylmetal hydride, **1**.[12] Scheme I shows how this intermediate is produced by oxidative addition of an allylic C–H bond to the metal. Oxidative addition of both C–C and C–H bonds was shown in I to be the initial step in the reaction of $Co^+$ with alkanes. Consequently, it seems a likely initial step for alkene systems. Reaction 5 is explained by β-hydrogen abstraction in **1** to form **2**, followed by reductive elimination of $H_2$.[13] This mechanism is analogous to that proposed previously for dehydrogenation of alkanes.[2,14]

The reduced reactivity of 2-methylpropene may simply be because dehydrogenation to form a cobalt ion–trimethylene methane complex is difficult. Another possibility is that substantial rearrangement is required before elimination of $H_2$ occurs. This could imply an increased lifetime for the $CoC_4H_8^+$ intermediate which is consistent with the higher abundance of the adduct observed in this system. One possible mechanism for a skeletal rearrangement of 2-methylpropene is outlined in Scheme II. Such a mechanism has been proposed as an initiation mechanism for olefin metathesis.[10,11,15] That metallacyclobutanes may rearrange to metal–olefin complexes via allylmetal hydrides is well supported.[16-18] Isomerization between **3** and **6** finds analogy with platinacyclobutane systems.[19-21] Indeed, the mechanism of this isomerization may very well be similar to that postulated for the

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[12] No distinction will be made in this paper between the syn and anti (shown) forms of the 1-methylallyl species, since their interconversion via a 1-butene complex is possible. However, it seems reasonable to speculate that reaction 5 probably occurs primarily through the anti isomer.

[13] The reverse of this process has been observed in solution by: Bertrand, J. A.; Jonassen, H. B.; Moore, D. W. *Inorg. Chem.* **1963**, *2*, 601. It is shown that reaction of hydridocobalt carbonyls with alkadienes yields π-allylcobalt carbonyls.

[14] Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332. Freas, R. B.; Ridge, D. P. *Ibid.* **1980**, *102*, 7129.

[15] Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1.

[16] Cushman, B. M.; Brown, D. B. *J. Organomet. Chem.* **1978**, *152*, C42.

[17] Johnson, T. H.; Cheng, S. *J. Am. Chem. Soc.* **1979**, *101*, 5277.

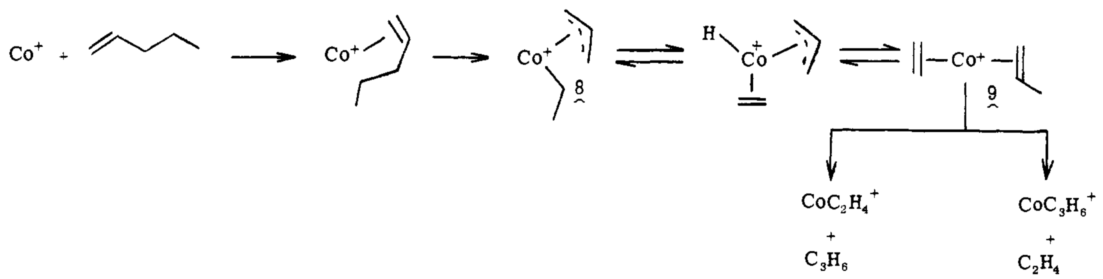
[18] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

[19] (a) AlEssa, R. J.; Puddephatt, R. J.; Tipper, C. F. H.; Thompson, P. J. *J. Organomet. Chem.* **1978**, *157*, C40. (b) AlEssa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Am. Chem. Soc.* **1979**, *101*, 364. (c) Perkins, D. C. L.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.* **1978**, *154*, C16. (d) Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Chem. Soc., Chem. Commun.* **1976**, 626.

[20] Johnson, T. H. *J. Org. Chem.* **1979**, *44*, 1356.

[21] Casey, C. P.; Scheck, D. M.; Shusterman, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 4233.

Scheme III



platinum complexes, via **5**, rather than via **4**.

Reactions 6 and 7 may also be explained by formation of metallacyclobutane intermediates. Ring cleavage in **6** may yield **7** which can then eliminate ethene, reaction 6. Both **3** and **6** can cleave to produce **4** which by sequential hydrogen abstractions can lead to reductive elimination of methane, reaction 7. Since this mechanism requires formation of a metallacyclobutane intermediate for all reactions in the 2-methylpropene system, the enhanced production of $CoC_2H_4^+$ and $CoC_3H_4^+$ compared to the linear butenes can be understood.

**Reaction of Co$^+$ with the Pentenes.** As with the butenes, two types of reactions are observed upon interaction of cobalt ions with the pentenes. Figure 3 shows the results and Table I summarizes the product distributions observed. Exothermic formation of cobalt ion-alkadiene complexes,[5] reactions 8 and 9, dominates the

$$Co^+ + C_5H_{10} \longrightarrow \begin{cases} CoC_5H_8^+ + H_2 & (8) \\ CoC_4H_6^+ + CH_4 & (9) \end{cases}$$

products of all systems but 1-pentene. In the latter case, the cleavage reactions 10 and 11 are the primary reaction pathways.

$$Co^+ + C_5H_{10} \longrightarrow \begin{cases} CoC_3H_6^+ + C_2H_4 & (10) \\ CoC_2H_4^+ + C_3H_6 & (11) \end{cases}$$

As with the mechanism proposed for the butenes, the first step in reaction of Co$^+$ with the pentenes is oxidative addition of an allylic C–C or C–H bond to the metal. All five pentenes can then undergo reaction 8 or 9 in analogy with Scheme I, although 1-pentene and 2-methyl-2-butene must presumably isomerize prior to producing $CoC_4H_6^+$. In analogy with Scheme II, reactions 10 and 11 may occur via formation of metallacyclobutane intermediates and subsequent ring cleavage. An alternate possibility, however, exists for the 1-pentene system. Scheme III shows that oxidative addition of the allylic C–C bond in 1-pentene produces **8**, an intermediate having an alkyl ligand with a hydrogen $\beta$ to the metal. Such an intermediate is not accessible in olefins having shorter carbon chains. Rapid $\beta$-H transfer to and from the metal, shown to occur in I,[22] yields the bis(olefin) complex **9**, which can decompose by loss of either alkene. This mechanism appears to be a much more facile route to cleavage than through metallacyclobutane species. For 2-pentene, reactions 10 and 11 probably occur as for 1-pentene; however, the need for prior isomerization (as in Scheme I) mediates the importance of this pathway. Presumably, the branched alkenes can cleave either as in Scheme II as noted above or by prior isomerization to 1-pentene, again as in Scheme II. Either mechanism, however, involves formation of a cobaltacyclobutane ion intermediate.

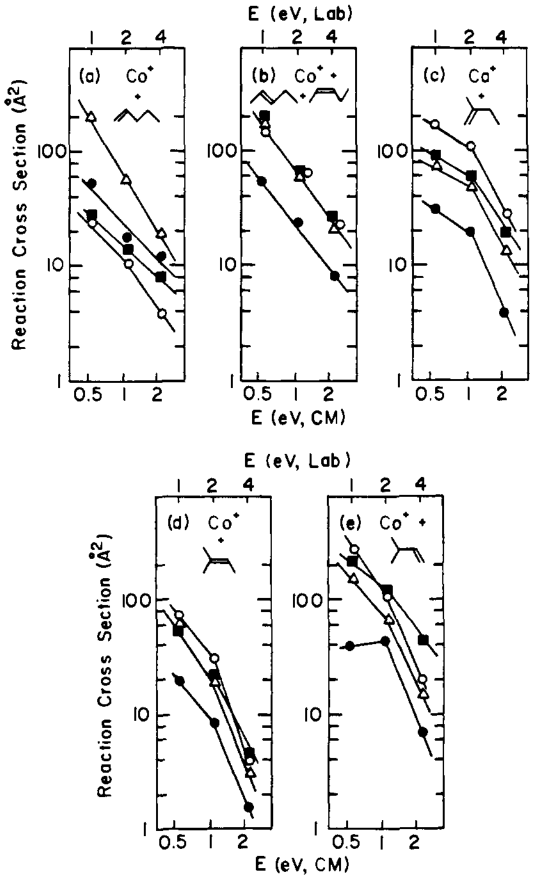


**Figure 3.** Variation in experimental cross section for the reactions of Co$^+$ with (a) 1-pentene, (b) a mixture of *cis*- and *trans*-2-pentene, (c) 2-methyl-1-butene, (d) 2-methyl-2-butene, and (e) 3-methyl-1-butene as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). Symbols represent the ionic products $CoC_5H_8^+$ (○), $CoC_4H_6^+$ (■), $CoC_3H_6^+$ (△), and $CoC_2H_4^+$ (●).

**Reactions of Co$^+$ with Hexenes.** The product distributions of the reactions of cobalt ions with 1-hexene and 2,3-dimethyl-2-butene are given in Table I. In general, the results are similar to analogous pentene systems. As with 1-pentene, cleavage processes dominate the 1-hexene reactions and presumably occur as in Scheme III. Alkadiene complexes dominate the products of the 2,3-dimethyl-2-butene system in analogy with the branched pentenes.

Several specific reactions of the hexenes deserve further comment. Reaction 12 is expected to be exothermic if the neutral

$$Co^+ + C_6H_{12} \rightarrow CoC_4H_6^+ + (C_2H_4 + H_2) \qquad (12)$$

product is ethane.[5] Since this process is endothermic for both hexenes, the neutral products shown are suggested. This implies $D^0(Co^+{-}C_4H_6) < 49$ kcal/mol[7] while from I, $D^0(Co^+{-}C_4H_6) > 45$ kcal/mol.[23] Reaction 13 requires that $D^0(Co^+{-}C_5H_8)$ be only

$$Co^+ + \text{1-hexene} \rightarrow CoC_5H_8^+ + CH_4 \qquad (13)$$

17 kcal/mol or more[7] to be exothermic. Thus, its apparent endothermicity suggests a high energy intermediate in the reaction mechanism.

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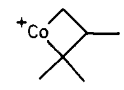
(22) See also Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445; **1979**, *101*, 4998.

(23) This conclusion is based on the exothermic formation of $CoC_4H_6^+$ from reaction of Co$^+$ with 2-methylbutane.[7]

The apparent endothermicity of reaction 14 poses another

$$Co^+ + (CH_3)_2C{=}C(CH_3)_2 \rightarrow CoC_3H_6^+ + C_3H_6 \quad (14)$$

interesting question since the metallacycle **10**, presumably can



**10**

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-

$$Co^+ + (CH_3)_2C{=}C(CH_3)_2 \rightarrow C_6H_{12}^+ + Co \quad (15)$$

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 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-

$$Co^+ + C_6H_{14} \rightarrow CoC_3H_6^+ + (C_3H_8) \quad (16)$$

methylbutane. These reactions, not explained in I, can occur via initial formation of $CH_4$ and $CoC_5H_{10}^+$. 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 $\beta$-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 slution-phase studies and the ease with which $\beta$-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.

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(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*).

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# 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 $Co(C_5H_6)^+$] and cyclohexane [yielding $Co(C_6H_8)^+$ and $Co(C_6H_6)^+$]. 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, none[12] 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

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(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.; Quyser, 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.

0002-7863/81/1503-6628$01.25/0