Thermochemistry and Structures of $CoC_3H_6^+$: Metallacycle and Metal−Alkene Isomers

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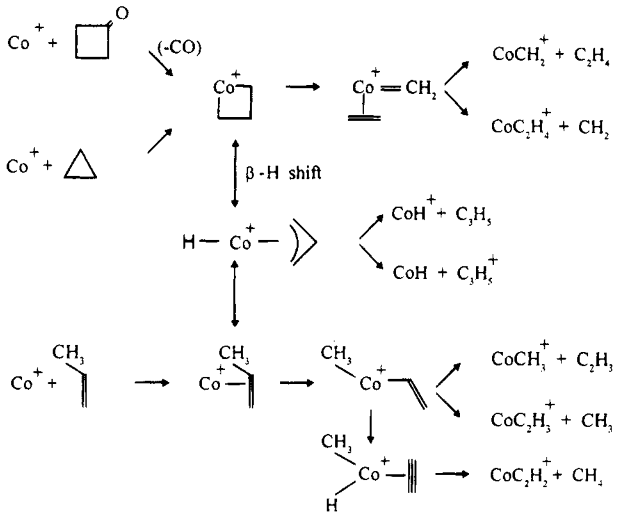
The thermochemistry for the metallacyclic and metal−alkene isomers of $CoC_3H_6^+$ is studied in a guided-ion-beam mass spectrometer. A flow-tube source is used to produce thermalized $CoC_3H_6^+$ ions formed by condensation of Co^+ with propene and cyclopropane, and by the decarbonylation of cyclobutanone by Co^+. These ions are then studied by threshold collisional activation and the results compared with the bimolecular reactivity of Co^+ with cyclopropane and propene. The results are interpreted to indicate that $CoC_3H_6^+$ ions formed in these three methods have both the Co^+—propene and cobaltacyclobutane ion structures in ratios of 100:0, 85:15, and 40:60, respectively. Some evidence for a third isomer, tentatively identified as the cobalt π-allyl hydrido ion complex, is also obtained. Reactivity and thermochemical differences of the ions produced in these three different ways are discussed and compared to previous work by other investigators and to work on these isomers of $FeC_3H_6^+$. Analysis of the kinetic energy dependence of the cross sections allows the determination of the 0 K bond dissociation energies: 1.87 ± 0.07 eV for Co^+—propene and 0.93 ± 0.07 eV for cobaltacyclobutane to dissociate and yield Co^+ + propene. We also determine 0 K bond dissociation energies for $Co^+—C_3H_5$, $Co^+—C_3H_4$ and $Co^+—C_2H_3$ to be 2.01 ± 0.17, 0.81 ± 0.09, and 2.10 ± 0.08 eV, respectively, and revise our reported 0 K bond energy for $Co^+—CH_2$ to 3.24 ± 0.06 eV.

Introduction

In a recent study, we used guided-ion-beam mass spectrometry to examine the thermochemistry and structure of two isomers of the $FeC_3H_6^+$ ion.[1] We determined that a metallacycle was formed from addition of Fe^+ and cyclopropane and in the decarbonylation reaction of Fe^+ with cyclobutanone, while the metal−alkene ion was generated as the adduct of Fe^+ and propene and in the dehydrogenation reaction of Fe^+ with propane. These isomers do not appear to interconvert readily, perhaps indicating a sizable barrier separating them. In this study, we extend this work to the analogous cobalt system. Despite the similarity that is often found between the chemistry of atomic iron and cobalt ions,[2] we find that the cobalt system behaves much differently than the iron system.

$CoC_3H_6^+$ ions are commonly observed as products in the reactions of Co^+ with straight-chain, branched-chain, and cyclic organic species. Reactions with straight- and branched-chain organic molecules appear to produce $CoC_3H_6^+$ ions with a Co^+—alkene structure,[3−6] while reactions with cyclic compounds are suggested to proceed via metallacyclic intermediates.[7−11] For example, the various products observed in the reaction of Co^+ with cyclopropane, studied first by Armentrout and Beauchamp[7] and later by Fisher and Armentrout,[11] can be explained if the reaction proceeds via the mechanism shown in Scheme 1.

Scheme 1



The bimolecular reactions of atomic ions with organic neutrals provide no thermochemical information regarding the $CoC_3H_6^+$ species because these species are either products of exothermic reactions or transiently formed intermediates. One means to obtain such thermochemical and structural information is to produce the

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ions and then probe them with additional reactions. Such studies were initially carried out by Jacobson and Freiser.[10] They showed that Fe^+ decarbonylates cyclobutanone to form a stable metallacyclobutane ion, a result that we subsequently verified by threshold collisional activation experiments.[1] Jacobson and Freiser also found that Co^+ decarbonylates cyclobutanone, but the ion formed appeared to have the Co^+–propene ion structure. They proposed that the cobaltacyclobutane ion initially formed has enough internal energy to rearrange to this Co^+–propene isomer through a π-allyl hydrido intermediate, as shown in Scheme 1. Studies by van Koppen *et al.*[12] have probed the structure of $CoC_3H_6^+$ ions by using both kinetic energy release distribution (KERD) analysis and high-energy collision-induced dissociation (CID). The KERDs allowed the 0 K heats of formation for the Co^+–propene and metallacycle structures to be determined as 247 ± 5 and 274 ± 5 kcal/mol, respectively.

In the experiments described in this paper, we generate the $CoC_3H_6^+$ ion by using the same reactions as van Koppen *et al.*[12] The ions are thermalized by forming them in a high-pressure flow tube, a process that is anticipated to cool the cobaltacyclobutane ions to the point where rearrangement to the lower energy Co^+–alkene complex may not occur. These ions are then probed by using threshold collisional activation (TCA),[1,13-15] where the $CoC_3H_6^+$ ions are activated by collisions with Xe and allowed to dissociate. The collision energy dependence for the various dissociation channels allows the thermochemistry to be measured. Comparison of this thermochemistry and the dissociation products to those observed in the bimolecular reaction of Co^+ with propene and cyclopropane allow the structures of the $CoC_3H_6^+$ ions to be assigned. This work provides consistent and complimentary results to the previous studies.

Experimental Section

The guided-ion-beam instrument on which these experiments were performed has been described in detail previously.[16,17] Ions are created in a flow-tube source as described below, extracted from the source, accelerated, and passed through a magnetic sector for mass analysis. The mass-selected ions are decelerated to the desired kinetic energy and focused into an octopole beam guide. This device uses radio-frequency electric fields to trap the ions in the radial direction and ensure complete collection of reactant and product ions.[18] The octopole passes through a gas cell of effective length 8.26 cm that contains the neutral collision partner at a pressure sufficiently low that multiple ion–molecule collisions are improbable. The unreacted parent and product ions drift to the end of the octopole from which they are extracted, passed through a quadrupole mass filter for mass analysis, and detected with a secondary electron scintillation ion detector using standard pulse counting techniques. Raw ion intensities are converted to cross sections as described previously.[16] We estimate absolute cross sections to be accurate to ±20%.

Laboratory (lab) energies are converted to energies in the center of mass (CM) frame by using the conversion $E_{CM} = E_{lab}M/(M + m)$, where m and M are the ion and neutral masses, respectively. The absolute energy scale and corresponding full width at half-maximum (fwhm) of the ion-beam kinetic energy distribution are determined by using the octopole as a retarding energy analyzer as described previously.[16] The absolute uncertainty in the energy scale is ±0.05 eV (lab). The energy distributions are nearly Gaussian and have a typical fwhm of 0.2–0.5 eV (lab).

Ion Sources. $CoC_3H_6^+$ ions are made in our flow-tube source, described in detail previously.[17] Co^+ is made by using a direct current discharge source[13] consisting of a cobalt cathode held at high negative voltage (1.5–3 kV) over which a flow of approximately 90% He and 10% Ar passes. Ar^+ ions created in the discharge are accelerated toward the cobalt cathode, sputtering off ionic and neutral metal atoms. An appropriate source gas, either propene, cyclopropane, or cyclobutanone, is added to the flow about 60 cm downstream of the discharge. (If these reagents are added too close to the discharge or if a high pressure of the hydrocarbon gas is used, hydrocarbon ions having the same mass as the desired $CoC_3H_6^+$ species are formed.) $CoC_3H_6^+$ ions are then formed by three-body collisions or bimolecular reactions. At typical flow-tube pressures of 0.5–0.6 Torr, the ions undergo $>10^4$ thermalizing collisions as they traverse the remaining 40 cm of the flow tube. Ions are extracted from the flow tube and gently focused through a 9.5 cm long differentially pumped region before entering the rest of the instrument described above. Before any experimental run, a high-energy (20–25 eV, lab) CID spectrum with Xe was taken in order to make sure that no impurity ions were present in the parent ion beam.

$CoC_3H_6^+$ ion beams produced as adducts of propene and cyclopropane were about 1 order of magnitude more intense than those generated from the reaction with cyclobutanone. This leads to somewhat noisier data in the latter system. It is possible that the Co^+ + cyclobutanone reaction could form $CoC_2H_2O^+$, which has the same mass as $CoC_3H_6^+$. Previous studies of the reaction of Co^+ with cyclobutanone did not report this product,[10,12] and we saw no evidence for its presence here either.

For studies involving the bimolecular reactions of Co^+ with cyclopropane and propene, Co^+ was made in the flow-tube discharge source, as described above for the cobalt complexes. To help quench any excited states of Co^+, we added approximately 1–3 mTorr of methane to the flow tube. The efficiency of this cooling was verified by a comparison with surface ionization (SI) results from previous work[11] and flow-tube results with and without methane added, including detailed threshold analyses of product cross sections, as described below. Co^+ ions made in the flow-tube discharge provide more intense beams than SI, which results in a higher sensitivity for minor products with cross-section magnitudes less than about 0.1 Å^2.

Thermochemical Analysis. Cross sections are modeled by using eq 1,[13,19] where E is the relative translational energy, E_0 is the reaction threshold at 0 K, E_{rot} is the average rotational energy (0.039 eV = $3k_BT/2$, T = 300 K) of the reactant ions, σ_0 is an energy-independent scaling parameter, and the exponent n is treated as a variable parameter.

$$\sigma = \sigma_0 \sum_i g_i(E + E_i + E_{rot} - E_0)^n/E \qquad (1)$$

Internal energies of the polyatomic reactants are included explicitly as a summation over vibrational energy levels, i, with energies E_i and relative populations g_i ($\sum g_i = 1$). We use the

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Table 1. Vibrational Frequencies (in cm^{-1})[a]

species	freq
propene[b]	174, 428, 578, 912, 920, 963, 991, 1045, 1171, 1297, 1378, 1420, 1443, 1470, 1650, 2871, 2932, 2954, 2991, 3013, 3090
$Co^+{-}$propene	A: free propene + 100, 300, 500 B: free propene + 100, 400, 700 C: free propene + 300, 500, 700
$\overline{Co^+{-}CH_2CH_2CH_2}$	common freq:[c] 535, 556, 627, 741, 749, 898, 926, 1001(2), 1219, 1222, 1223, 1257(2), 1260, 1443, 1447, 2887, 2893, 2895, 2952, 2975, 2987 A: common freq + 1443 B: common freq + 197

[a] Degeneracies in parentheses. [b] Reference 21. [c] Reference 22.

Beyer–Swinehart algorithm[20] to calculate a Maxwell–Boltzmann distribution of vibrational energies at 300 K which is used for the factors g_i in eq 1. We have described this modeling procedure in detail elsewhere.[13]

The vibrational frequencies of the $CoC_3H_6^+$ complexes are determined similarly to the procedure of van Koppen *et al.*[12] and that in our study of $FeC_3H_6^+$ isomers.[1] Here, vibrational frequencies of the free ligand are used, along with values for the modes involving Co^+ that are at the limits of what is reasonable. For the $Co^+{-}$propene structure, propene frequencies were used[21] along with several possible estimates for the $Co^+{-}C_3H_6$ modes. For the cobaltacyclobutane ion, cyclopropane frequencies[22] were used along with $Co^+{-}C$ frequencies taken from a matrix study of a Fe–cyclopropane complex,[23] as was done in our previous work on $FeC_3H_6^+$.[1] The values used for the vibrational levels are summarized in Table 1. Because these species have few low-frequency modes, the exact choice of vibrational frequencies is not critical. The average vibrational energy at 300 K for the cobaltacyclobutane ion is only about 0.04 eV, and that for the cobalt–propene ion is only about 0.07 eV.

In the bimolecular reactions of Co^+ with cyclopropane and propene, the internal energy of the reactants is just the average rotational (0.039 eV) and vibrational energies (0.016 and 0.036 eV for cyclopropane and propene, respectively). As discussed further below, our results for Co^+ produced in the flow tube with methane added are consistent with ions that have little electronic excitation. For the TCA experiments where we have no information regarding the electronic states of the cobalt ion–hydrocarbon complexes, we ignore electronic excitation. It seems likely that the population of any electronic levels has equilibrated to the 300 K temperature of the flow gas, such that the average electronic energy is negligible. Even if the distribution is somewhat hotter, it seems unlikely that the contributions of electronic excitation will influence the thresholds determined here outside of the error limits provided.

Comparisons of the thresholds derived here to our previous work is complicated by differing assumptions made concerning interpretation of the thresholds. Previously, we ignored the internal energy contributions of the neutral reactants, although the electronic energies were considered in detail. To compare to the present 0 K thresholds, we simply correct the previously determined thresholds by adding the average rotational and vibrational energies of the reactants. This is discussed in more detail elsewhere.[24]

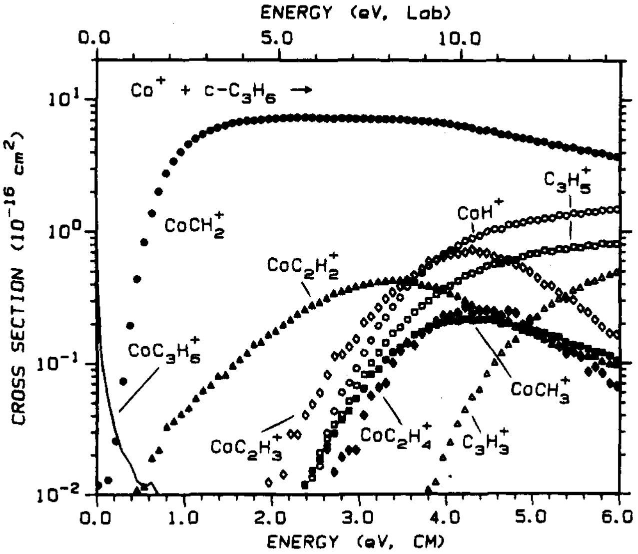

Figure 1. Cross sections for the bimolecular reaction of Co^+ with cyclopropane as a function of relative energy (lower x axis) and laboratory energy (upper x axis). The cross section for $CoC_3H_6^+$ (solid line) is obtained at a cyclopropane pressure of 0.2 mTorr.

The hydrocarbon gases were obtained from Matheson in high purity (>99%) and were used without further purification. Cyclobutanone (99%, Aldrich) and Xe (99.995%, Air Products) were used without further purification, except for multiple freeze–pump–thaw cycles to remove noncondensible impurities.

Results

Bimolecular Reactions. Co^+ + Cyclopropane. The major products for the bimolecular reaction of Co^+ with cyclopropane are shown in Figure 1 and correspond to reactions 2-10. The 0 K thermochemistry indicated

$$Co^+ + \text{cyclopropane} \rightarrow CoC_3H_6^+ \quad (2)$$

$$\rightarrow CoC_2H_4^+ + CH_2 - (2.07 \pm 0.08\ \text{eV}) \quad (3)$$

$$\rightarrow CoC_2H_3^+ + CH_3 \quad (4)$$

$$\rightarrow CoC_2H_2^+ + CH_4 + 0.49\ \text{eV} \quad (5)$$

$$\rightarrow CoCH_3^+ + C_2H_3 - (1.87 \pm 0.06\ \text{eV}) \quad (6)$$

$$\rightarrow CoCH_2^+ + C_2H_4 - (0.67 \pm 0.10\ \text{eV}) \quad (7)$$

$$\rightarrow CoH^+ + c\text{-}C_3H_5 - (2.57 \pm 0.06\ \text{eV}) \quad (8)$$

$$\rightarrow c\text{-}C_3H_5^+ + CoH - (3.00 \pm 0.07\ \text{eV}) \quad (9)$$

$$\rightarrow C_3H_3^+ + CoH + H_2 - (4.06 \pm 0.14\ \text{eV}) \quad (10)$$

with the reactions is determined from literature information in Tables 2 and 3. Other products observed, all with cross-section magnitudes less than 0.1 Å² and therefore not shown in Figure 1 for clarity, are CH_3^+, $C_2H_3^+$, $CoC_3H_3^+$, $CoC_3H_4^+$, and $CoC_3H_5^+$.

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Table 2. Literature Thermochemistry

species	$\Delta_f H°_0$, kcal/mol	$\Delta_f H°_{298}$, kcal/mol
H	51.634 ± 0.001^{a}	52.103 ± 0.001^{a}
CO	-27.20 ± 0.04^{a}	-26.42 ± 0.04^{a}
CH_2	92.8 ± 0.6^{b}	92.9 ± 0.6^{c}
CH_3	35.8 ± 0.1^{b}	35.0 ± 0.1^{d}
CH_4	-15.9 ± 0.1^{b}	-17.8 ± 0.1^{e}
C_2H_2	54.7 ± 0.2^{b}	54.5 ± 0.2^{e}
C_2H_3	72.6 ± 0.8^{f}	71.6 ± 0.8^{f}
C_2H_4	14.6 ± 0.1^{b}	12.5 ± 0.1^{e}
C_3H_3	83 ± 2^{g}	82 ± 2^{h}
$C_3H_3^+$	283 ± 3^{g}	$283 \pm 3^{h,i}$
c-C_3H_3	106 ± 4^{g}	105 ± 4^{h}
c-$C_3H_3^+$	258 ± 2^{g}	$258 \pm 2^{h,i}$
C_3H_4 (propyne)	46.2 ± 0.5^{b}	44.2 ± 0.2^{e}
C_3H_4 (allene)	47.7 ± 0.3^{b}	45.6 ± 0.2^{e}
C_3H_5	43.5 ± 2.1^{d}	40.9 ± 2.1^{d}
$C_3H_5^+$	231.0 ± 2.2^{j}	$229.4 \pm 2.1^{i,j}$
c-C_3H_5	70.0 ± 0.3^{k}	66.9 ± 0.3^{l}
c-$C_3H_5^+$	258.6 ± 0.8^{k}	$257.0 \pm 0.8^{i,m}$
C_3H_6 (propene)	8.4 ± 0.2^{b}	4.8 ± 0.2^{e}
c-C_3H_6	16.8 ± 0.1^{b}	12.7 ± 0.1^{e}
c-C_4H_6O	-16 ± 2^{n}	-21 ± 2^{o}
Co	101.6 ± 0.5^{a}	102.0 ± 0.5^{a}
Co^+	283.0 ± 0.5^{a}	284.8 ± 0.5^{a}

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The adduct, $CoC_3H_6^+$, has a cross section that depends linearly on cyclopropane pressure, indicating that it is formed by stabilizing secondary collisions. Cross-section features that are linearly dependent on reactant pressure are also observed for the $CoC_2H_4^+$ and $CoC_2H_3^+$ products at low energies. The energy dependence of these features suggests that they are due to a secondary reaction of the large $CoCH_2^+$ primary product. No other cross sections were found to be pressure dependent in this system. In Figure 1, the $CoC_2H_4^+$ and $CoC_2H_3^+$ cross sections shown have been extrapolated to zero-pressure (rigorously single-collision) conditions.

The results obtained from this bimolecular reaction are consistent with the limited results of Armentrout and Beauchamp[7] and the more extensive work of Fisher and Armentrout,[11] where Co^+ was produced by surface ionization. Four differences with the previous work are noted. First, the cross sections measured here are all about 35 ± 10% larger than those of Fisher and Armentrout and are comparable to those measured by Armentrout and Beauchamp. These variations in absolute magnitudes are within the experimental errors of these measurements. Second, minor products with relatively low cross sections are observed here due to a larger reactant ion intensity. Third, this intensity also permitted higher mass resolution conditions that allowed us to resolve the $CoCH_3^+$ product from the much more intense $CoCH_2^+$ product and the $CoC_2H_3^+$ from the $CoC_2H_2^+$ and $CoC_2H_4^+$ products. Finally, the cross section for the $CoCH_2^+$ product reported by Armentrout and Beauchamp and by Fisher and Armentrout is nonzero (~1.0 and ~0.4 Å^2, respectively) at the lowest kinetic energies, in contrast to the results here. This is an indication of a colder ion beam, as discussed further in the threshold analysis section below.

Co^+ + Propene. The major products for the bimolecular reaction of Co^+ with propene are shown in Figure 2. Products observed correspond to reactions 11−20. A

$$\mathrm{Co^+ + propene \rightarrow CoC_3H_6^+} + (1.91 \pm 0.22\ \mathrm{eV}) \tag{11}$$

$$\rightarrow \mathrm{CoC_3H_5^+ + H} \tag{12}$$

$$\rightarrow \mathrm{CoC_3H_4^+ + H_2} \tag{13}$$

$$\rightarrow \mathrm{CoC_2H_3^+ + CH_3} \tag{14}$$

$$\rightarrow \mathrm{CoC_2H_2^+ + CH_4} + 0.12\ \mathrm{eV} \tag{15}$$

$$\rightarrow \mathrm{CoCH_3^+ + C_2H_3} - (2.24 \pm 0.06\ \mathrm{eV}) \tag{16}$$

$$\rightarrow \mathrm{CoCH_2^+ + C_2H_4} - (1.03 \pm 0.10\ \mathrm{eV}) \tag{17}$$

$$\rightarrow \mathrm{CoH^+ + C_3H_5} - (1.78 \pm 0.11\ \mathrm{eV}) \tag{18}$$

$$\rightarrow \mathrm{C_3H_5^+ + CoH} - (2.17 \pm 0.10\ \mathrm{eV}) \tag{19}$$

$$\rightarrow \mathrm{C_3H_3^+ + CoH + H_2} - (4.42 \pm 0.14\ \mathrm{eV}) \tag{20}$$

number of minor products, not shown for clarity, include CH_3^+, $C_2H_3^+$, $C_3H_6^+$, $CoC_2H_4^+$, $CoC_3H_2^+$, and $CoC_3H_3^+$. All have maximum cross-section magnitudes less than 0.1 Å^2. The product with the largest cross section is the $CoC_3H_6^+$ adduct formed in reaction 11. Its cross section depends linearly on pressure, indicating that this product is stabilized by secondary collisions. No other products had cross sections that were pressure-dependent.

It is interesting to note that the amount of the $CoC_3H_6^+$ adduct formed in this system is much larger than that observed in the bimolecular reaction of Co^+ with cyclopropane at the same neutral pressure (Figures 1 and 2). This observation either indicates that the Co^+—propene adduct is much more stable than the Co^+—cyclopropane adduct or that Co^+ induces a rearrangement of the cyclopropane to the more stable propene isomer and the energy released in this isomerization reduces the lifetime of the Co^+—propene isomer formed in the cyclopropane system.

Threshold Collisional Activation Studies. $CoC_3H_6^+$ (from Propene) + Xe. Cross sections for interaction of Xe with $CoC_3H_6^+$ made by adding propene

Table 3. Cobalt–Ligand Bond Dissociation Energies (in eV) at 0 K

species	bond energy
Co^+–propene	$1.87 \pm 0.07,^a$ 1.91 ± 0.22^b
Co^+–$CH_2CH_2CH_2$	$0.93 \pm 0.07,^{a,c}$ $0.75 \pm 0.22^{c,d}$
Co^+–C_3H_5	2.01 ± 0.18^a
Co^+–C_3H_4	$\geq 0.82 \pm 0.09^{a,e}$
Co^+–C_2H_4	$1.86 \pm 0.07,^f$ 1.82 ± 0.22^b
Co^+–C_2H_3	2.10 ± 0.08^a
Co^+–C_2H_2	$\geq 0.28 \pm 0.13,^a$ $>0.36 \pm 0.15,^g$ $1.44,^h$ $\sim 1.72^i$
Co^+–CH_2	$3.24 \pm 0.06,^a$ $3.26 \pm 0.10,^g$ 3.43 ± 0.17^j
Co^+–CH_3	2.10 ± 0.04^k
Co^+–H	1.98 ± 0.06^k
Co–H	1.86 ± 0.05^k

[a] This work. [b] Reference 27. [c] Dissociation to Co^+ + propene. [d] Calculated from $\Delta_f H°_0$(cobaltacyclobutane) given in ref 27 and Table 2. [e] Assuming a propyne structure. The bond energy is $\geq 0.88 \pm 0.09$ eV if the C_3H_4 structure is allene. [f] Reference 30. [g] Reference 11. [h] Reference 26. [i] Best estimate; see text. [j] Reference 25. [k] Reference 24.

to the flow tube are shown in Figure 3. The products observed correspond to reactions 21–28.

$$CoC_3H_6^+ + Xe \rightarrow Co^+ + C_3H_6 + Xe - (1.91 \pm 0.22\ \text{eV}) \quad (21)$$

$$\rightarrow CoXe^+ + C_3H_6 \quad (22)$$

$$\rightarrow CoC_2H_3^+ + CH_3 + Xe \quad (23)$$

$$\rightarrow CoCH_3^+ + C_2H_3 + Xe - (4.15 \pm 0.23\ \text{eV}) \quad (24)$$

$$\rightarrow CoCH_2^+ + C_2H_4 + Xe - (2.94 \pm 0.24\ \text{eV}) \quad (25)$$

$$\rightarrow CoH^+ + C_3H_5 + Xe - (3.69 \pm 0.25\ \text{eV}) \quad (26)$$

$$\rightarrow C_3H_5^+ + CoH + Xe - (4.08 \pm 0.24\ \text{eV}) \quad (27)$$

$$\rightarrow C_3H_3^+ + CoH + H_2 + Xe - (6.33 \pm 0.26\ \text{eV}) \quad (28)$$

A minor product, $CoC_2H_2^+$, is not shown due to its relatively small cross section, about 0.01 Å^2 at 15 eV. The predominant product at all energies is simple collision-induced dissociation (CID) to form Co^+ (reaction 21). The main feature in this product cross section rises from an apparent threshold between 1 and 2 eV to reach a maximum cross section of about 7 Å^2 above 6 eV. At low energies, there is also a very small feature in the Co^+ cross section that has a threshold of several tenths of an electronvolt. It was verified that this feature is not dependent on the pressure of Xe and that it is reproducible. The only other low-energy channel is ligand exchange to form $CoXe^+$ (reaction 22). At energies above 4 eV, several other products formed in reactions 23–28 are also observed. Note that these correspond to the primary products observed in the bimolecular reaction of Co^+ with propene. All six of these products rise from thresholds that are well above the thermodynamic thresholds and have cross sections with maximum magnitudes of 0.4 Å^2 or less.

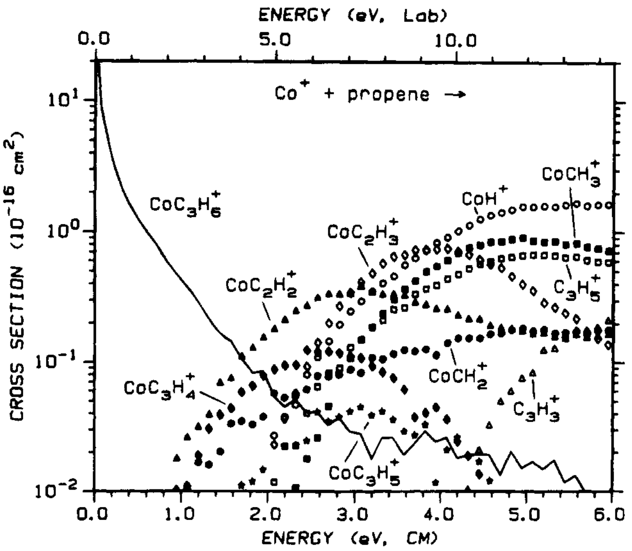

Figure 2. Cross sections for the bimolecular reaction of Co^+ with propene as a function of relative energy (lower *x* axis) and laboratory energy (upper *x* axis). The cross section for $CoC_3H_6^+$ (solid line) is obtained at a propene pressure of 0.2 mTorr.

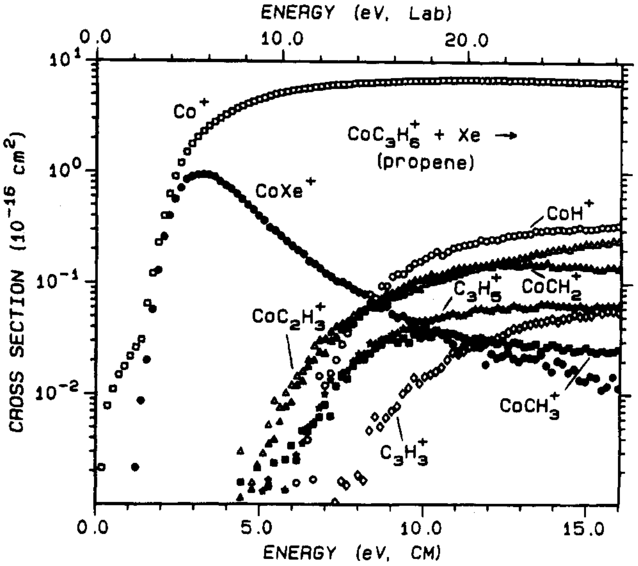

Figure 3. Cross sections for TCA of $CoC_3H_6^+$ (made by adding propene to the flow tube) with xenon as a function of relative energy (lower *x* axis) and laboratory energy (upper *x* axis).

$CoC_3H_6^+$ (from Cyclopropane) + Xe. Cross sections for the interaction of Xe with $CoC_3H_6^+$ formed by adding cyclopropane to the flow tube are shown in Figure 4. Close inspection reveals that these results are nearly identical with those of Figure 3. The same products are observed with cross sections having similar thresholds and magnitudes. The only exception is the $CoCH_2^+$ cross section, which exhibits a low-energy feature beginning at about 3 eV that is not present in Figure 3.

$CoC_3H_6^+$ (from Cyclobutanone) + Xe. Cross sections for interaction of Xe with $CoC_3H_6^+$ formed by adding cyclobutanone to the flow tube are shown in Figure 5. Other products, $C_3H_3^+$, $C_3H_5^+$, and $CoCH_3^+$, were also observed; however, due to the smaller reactant beam intensity, the cross sections for these products are noisy and are not shown for clarity. Co^+ and $CoXe^+$ are again the main reaction products, but both products rise from apparent thresholds that are lower in energy than in the previous two systems. Both CoH^+ and $CoC_2H_3^+$ rise from thresholds that are about the same as those

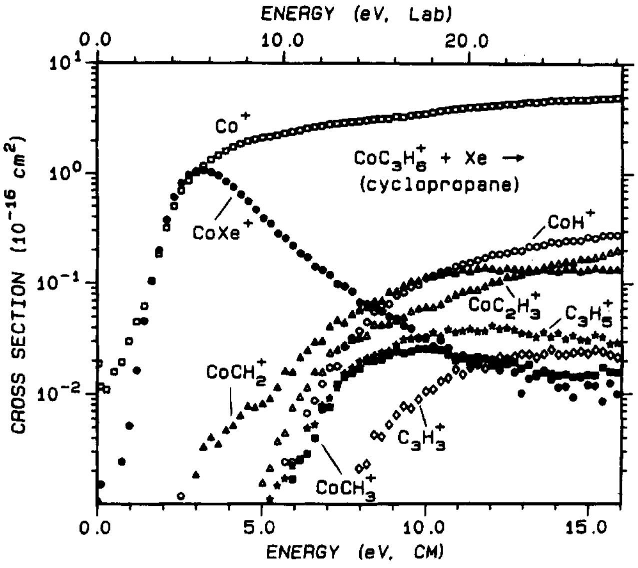

Figure 4. Cross sections for TCA of $CoC_3H_6^+$ (made by adding cyclopropane to the flow tube) with xenon as a function of relative energy (lower x axis) and laboratory energy (upper x axis).

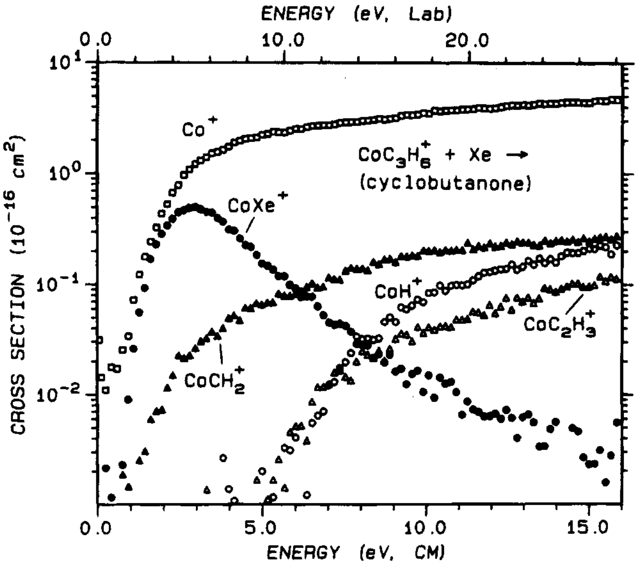

Figure 5. Cross sections for TCA of $CoC_3H_6^+$ (made by decarbonylation of cyclobutanone in the flow tube) with xenon as a function of relative energy (lower x axis) and laboratory energy (upper x axis).

in Figures 3 and 4, but the magnitudes of these products are a factor of about 2 smaller, as confirmed by more detailed analysis of the cross sections with eq 1. The most obvious difference between these results and those of Figures 3 and 4 is the cross section of the $CoCH_2^+$ product, which now rises from an apparent threshold of about 1 eV, much lower than that observed in the two previous systems.

Thermochemistry. Bimolecular Reactions. Cross sections for reaction of Co^+ with cyclopropane and propene were analyzed with eq 1. The optimum parameters are reported in Table 4. For most products (exceptions are CoH^+ and $C_3H_5^+$), the thresholds in the two systems are shifted by the difference in the heats of formation of propene and cyclopropane (0.36 eV; Table 2). This indicates that the products are the same in both reactions. Individual products where new thermodynamic information is derived are discussed below.

Table 4. Parameters Used in Eq 1 for Fitting Co^+ Bimolecular Reaction Cross Sections

product	n	σ_0	E_0, eV	E_0(lit.),[a] eV
		Co^+ + Cyclopropane		
$C_3H_3^+$	1.5 ± 0.2	1.22 ± 0.19	4.14 ± 0.09	4.06 ± 0.14
c-$C_3H_5^+$	2.0 ± 0.3	0.52 ± 0.22	2.50 ± 0.13	3.00 ± 0.07
CoH^+	1.8 ± 0.2	1.53 ± 0.25	2.82 ± 0.07	2.57 ± 0.06
$CoCH_2^+$ [b]	0.8 ± 0.1	10.58 ± 0.57	0.68 ± 0.04	0.67 ± 0.10
$CoCH_2^+$ [c]	0.8 ± 0.1	10.03 ± 1.26	0.70 ± 0.04	
$CoCH_3^+$	2.5 ± 0.6	0.19 ± 0.10	2.16 ± 0.21	1.87 ± 0.06
$CoC_2H_2^+$	2.4 ± 0.4	0.14 ± 0.07	0.71 ± 0.18	
$CoC_2H_3^+$	2.9 ± 0.2	0.25 ± 0.06	1.84 ± 0.07	
$CoC_2H_4^+$	3.1 ± 0.5	0.16 ± 0.10	2.29 ± 0.19	2.07 ± 0.08
		Co^+ + Propene		
$C_3H_3^+$	1.0 ± 0.2	0.90 ± 0.08	4.72 ± 0.15	4.42 ± 0.14
$C_3H_5^+$	2.0 ± 0.2	0.40 ± 0.06	2.20 ± 0.07	2.17 ± 0.10
CoH^+	2.3 ± 0.3	0.66 ± 0.24	2.08 ± 0.16	1.78 ± 0.11
$CoCH_2^+$	1.8 ± 0.2	0.08 ± 0.02	0.98 ± 0.14	1.03 ± 0.10
$CoCH_3^+$	2.2 ± 0.4	0.69 ± 0.26	2.38 ± 0.18	2.24 ± 0.06
$CoC_2H_2^+$	2.1 ± 0.3	0.24 ± 0.06	1.00 ± 0.12	
$CoC_2H_3^+$	1.8 ± 0.3	1.33 ± 0.23	2.28 ± 0.09	
$CoC_3H_4^+$	2.0 ± 0.3	0.08 ± 0.02	0.82 ± 0.09	
$CoC_3H_5^+$	1.1 ± 0.1	0.10 ± 0.05	1.75 ± 0.15	

[a] Calculated by using data in Tables 2 and 3. [b] Data analyzed assuming a 300 K distribution of electronic states. [c] Data analyzed allowing the distribution of electronic states to vary. The optimum electronic temperature was 800 ± 100 K.

CoH^+ and CoH. The formations of $CoH^+ + C_3H_5$ and $C_3H_5^+$ + CoH in the bimolecular reaction of Co^+ + cyclopropane have measured thresholds that are most consistent with producing the cyclic isomers of the C_3H_5 neutral and cation (Table 4). Production of allyl radical and allyl ion would occur ~1.2 eV lower in energy than for the cyclic C_3H_5 isomers. Fisher and Armentrout[11] drew the same conclusion. These results indicate that the reactions proceed primarily by C—H bond activation of the cyclopropane, a step not indicated in Scheme 1. However, both cross sections, particularly the $C_3H_5^+$ product, exhibit small tails (<0.1 Å^2) at lower energies. This is responsible for the measurement of a threshold for the $C_3H_5^+$ + CoH product channel that is somewhat lower than the calculated thermodynamic threshold (Table 4). These tails probably indicate that allylic isomers are produced with low probability.

In the propene system, the $CoH^+ + C_3H_5$ and $C_3H_5^+$ + CoH product cross sections rise from thresholds that are lower than in the cyclopropane system and that are consistent with production of the allyl radical and cation isomers. These processes can occur as indicated in Scheme 1 by activation of the allylic C—H bond of propene.

$CoCH_2^+$. As noted above, the cross section for production of $CoCH_2^+$ in the bimolecular reaction of Co^+ with cyclopropane differs from that determined by Fisher and Armentrout[11] at the lowest energies. This difference can be attributed to changes in the electronic state distribution of the Co^+ reactant in the two studies. When they are formed by surface ionization at 2250 K, 84% of the Co^+ ions are in their a^3F ground state (with an average energy for the various spin—orbit levels of 0.055 eV), 16% are in the a^5F first excited state (average energy 0.483 eV), and 0.2% are in the b^3F state (average energy 1.30 eV).[11] When Co^+ is formed in the dc discharge/flow-tube source, the results for reaction 7 depend on the flow gases present. Figure 6 compares these results for various flow conditions to the previous SI data. In all cases, Co^+ ions produced in the flow tube have a $CoCH_2^+$ cross section smaller than for Co^+ (SI) at the lowest kinetic energies. As the percentage of Ar added to the flow tube is increased, the cross section

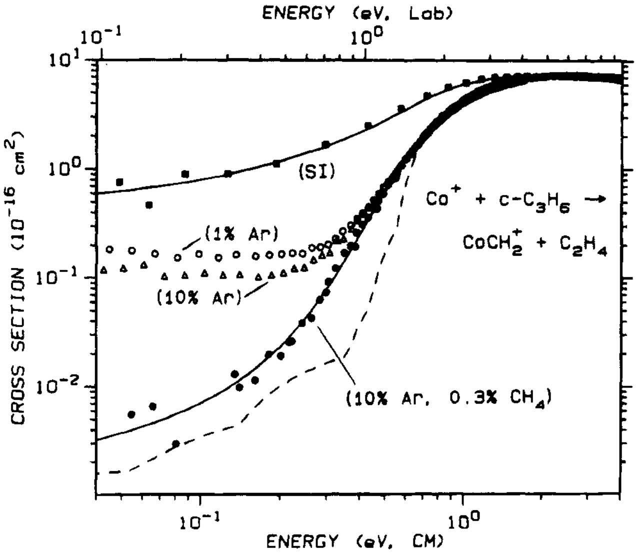

Figure 6. $CoCH_2^+$ product cross sections from the bimolecular reaction of Co^+ + cyclopropane. Solid squares represent data taken with Co^+ ions made by surface ionization (SI) at a filament temperature of 2250 ± 100 K, scaled by 35% to match the present data at higher energies. Also shown are data for Co^+ ions made in the dc discharge/flow-tube source with flow mixtures of 1% Ar–99% He (open circles), 10% Ar–90% He (open triangles), and 10% Ar–90% He–0.3% CH_4 (solid circles). The dashed line shows the optimum model for the $CoCH_2^+$ cross section with a Co^+ electronic state distribution characteristic of 800 K. The solid line is this model convoluted over the experimental kinetic energy distributions. The line through the SI data is the convoluted model with a Co^+ electronic state distribution characteristic of 2250 K.

below 0.4 eV decreases and virtually disappears when a small amount of CH_4 is added to the flow. These observations are rationalized if the Ar and CH_4 gases quench the excited electronic states of Co^+.

To obtain thermodynamic information regarding $CoCH_2^+$, we analyzed only data where both Ar and CH_4 are present in the flow tube. We assumed that the a^3F ground and a^5F first excited states of Co^+ have comparable reactivities. When we assume the population of these states to correspond to a 300 K distribution, we obtain the optimum parameters for eq 1 given in Table 4, including $E_0 = 0.68 \pm 0.04$ eV. This model did not reproduce the cross section at the lowest experimental energies. We therefore allowed the temperature of the electronic state distribution to vary. The best reproduction of the data was obtained when the population of the Co^+ states corresponded to a 800 K distribution (where 99.7% of the ions are in the a^3F state and 0.3% are in the a^5F state). This model is shown in Figure 6, and the optimum parameters of eq 1, including $E_0 = 0.70 \pm 0.04$ eV, are given in Table 4. If the electronic temperature is increased to 2250 K, the same model also reproduces the SI data, as shown in Figure 6. For comparison, the threshold derived by Fisher and Armentrout,[11] which includes corrections for the presence of the a^3F, a^5F, and b^3F states, can be adjusted to 0 K to yield $E_0 = 0.73 \pm 0.07$ eV, in good agreement with the present result.

We conservatively take the average of the two threshold measurements (300 K assumption and variable-temperature assumption) as our best determination. This threshold, 0.69 ± 0.06 eV, leads to a $CoCH_2^+$ bond dissociation energy (BDE) at 0 K of 3.24 ± 0.06 eV. This value is preferred to those we have published previously, because analysis of the present result is less dependent on assumptions regarding the relative reactivities of the various electronic states of Co^+. This BDE can be compared favorably with a value of 3.43 ± 0.17 eV obtained by ab initio calculations.[25] Other literature values are also consistent and have been discussed in detail previously.[11]

Analysis of the $CoCH_2^+$ cross section in the Co^+ + propene reaction system is difficult, because the cross section has a fairly complicated shape. The initial rise in the cross section can be modeled by the parameters in Table 4 with a threshold consistent with the calculated thermochemical value. This demonstrates that reaction 17 does produce ethene as the neutral product.

$CoC_2H_2^+$. One of the major products observed at low energies in both bimolecular reaction systems is $CoC_2H_2^+$. To have such a low threshold, this product must be accompanied by CH_4. Sodupe and Bauschlicher[26] have calculated the Co^+—C_2H_2 BDE to be 1.44 eV, which means that reactions 5 and 15 are exothermic. The observation of a threshold in both reactions is therefore attributable to a barrier along the reaction path. The threshold measurements are consistent and indicate that the barrier lies 1.00 ± 0.12 eV (1.07 ± 0.18 eV from the cyclopropane system) above the Co^+ + propene asymptote. This is also consistent with the previous measurement of Fisher and Armentrout,[11] although they erroneously reported that this threshold leads to $D(Co^+{-}C_2H_2) > 1.47 \pm 0.15$ eV instead of $>0.36 \pm 0.15$ eV, due to a mathematical miscalculation. The thresholds measured here lead to a lower limit for $D_0(Co^+{-}C_2H_2) \geq 0.28 \pm 0.13$ eV.

$CoC_2H_3^+$. Co^+—C_2H_3 is formed in both reactions 4 and 14 in the bimolecular reaction of Co^+ with cyclopropane and propene. Combining the thresholds measured (Table 4) with the appropriate hydrocarbon thermochemistry from Table 2, we find $D_0(Co^+{-}C_2H_3) = 2.13 \pm 0.08$ and 2.06 ± 0.10 eV, respectively. We take the average of these two numbers as our best determination and report $D_0(Co^+{-}C_2H_3) = 2.10 \pm 0.08$ eV. There are no previously measured values for comparison, but this value is comparable to $D_0(Fe^+{-}C_2H_3) = 2.5 \pm 0.1$ eV obtained by Schultz and Armentrout,[1] after correcting to 0 K. It is also comparable to $D_0(Co^+{-}CH_3)$ (Table 3), consistent with a largely covalent Co^+—C_2H_3 interaction, as discussed more thoroughly elsewhere.[24]

$CoC_3H_4^+$. This product ion is formed in reaction 13, dehydrogenation of propene by Co^+. It is unknown whether the C_3H_4 species has an allene or propyne structure. From the threshold measured for this reaction (Table 4), a Co^+—propyne BDE of 0.82 ± 0.09 eV or a Co^+—allene BDE of 0.88 ± 0.09 eV is determined. These values are well below those for Co^+—propene (Table 2) and are likely to be lower limits.

$CoC_3H_5^+$. The Co^+—C_3H_5 BDE can also be obtained from the bimolecular reaction of Co^+ with propene (reaction 12). The threshold of 1.75 ± 0.15 eV (Table 4) combined with $D_0(H{-}C_3H_5) = 3.76 \pm 0.09$ eV (Table 2) leads to $D_0(Co^+{-}C_3H_5) = 2.01 \pm 0.18$ eV. This is comparable to $D_0(Co^+{-}CH_3)$ and slightly greater than $D_0(Co^+{-}C_3H_6)$, such that the energy measured could be

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(25) Bauschlicher, C. W., Jr.; Partridge, H.; Sheehy, J. A.; Langhoff, S. R.; Rosi, M. *J. Phys. Chem.* **1992**, *96*, 6969.

(26) Sodupe, M.; Bauschlicher, C. W. *J. Phys. Chem.* **1991**, *95*, 8640. $D(Co^+{-}C_2H_2)$ is uncorrected from the D_e value, as discussed in this reference.

Table 5. Parameters Used in Eq 1 for Fitting Co^+ TCA Reaction Cross Sections

product	n	σ_0	E_0, eV	E_0(lit.),[a] eV
		$CoC_3H_6^+$ (Propene)		
Co^+	1.4 ± 0.1	3.94 ± 0.43	1.87 ± 0.07	1.91 ± 0.22
$CoXe^+$	0.7 ± 0.3	2.86 ± 0.37	2.09 ± 0.11	
$CoCH_2^+$	2.0 ± 0.2	0.04 ± 0.01	5.03 ± 0.15	
		$CoC_3H_6^+$ (Cyclopropane)		
Co^+	1.4 ± 0.1	3.70 ± 0.69	1.83 ± 0.08	
$CoCH_2^+$	1.7 ± 0.2	0.004 ± 0.002	1.75 ± 0.20	
		$CoC_3H_6^+$ (Cyclobutanone)		
Co^+	2.2 ± 0.1	1.02 ± 0.16	0.89 ± 0.06	0.74 ± 0.22
Co^+ [b]	1.7 ± 0.1	1.04 ± 0.09	0.93 ± 0.07	0.74 ± 0.22
$CoCH_2^+$ [c]	1.5 ± 0.1	0.06 ± 0.02	1.49 ± 0.14	
$CoCH_2^+$ [d]	1.0	0.02	1.1 ± 0.1	

[a] Calculated by using data in Tables 2 and 3. [b] Data analyzed after accounting for a contribution from the Co^+—propene isomer; see text. [c] Data analyzed over the entire energy range studied. [d] Data analyzed after accounting for contributions from other $CoC_3H_6^+$ isomers; see text.

consistent with a covalent $Co^+—CH_2CH=CH_2$ bond or a dative Co^+—allyl interaction.

Threshold Collisional Activation Studies. The thresholds measured for the various products observed at high energy in the three threshold collisional activation studies are about 1−2 eV higher than the calculated thresholds. This is probably due to the severe competition between these complicated rearrangement reactions and the simple CID process to eliminate C_3H_6 that dominates the product spectrum. Analysis with eq 1 verifies that the thresholds for the various product ions are the same in all three systems except for CID, ligand exchange, and the $CoCH_2^+$ products.

$Co^+—C_3H_6$. We measure 0 K thresholds of 1.87 ± 0.07, 1.83 ± 0.08, and 0.89 ± 0.06 eV for the dissociation of $Co^+—C_3H_6$ to Co^+ in the propene, cyclopropane, and cyclobutanone systems, respectively (Table 5). The threshold obtained in the propene system should be a direct measure of the Co^+—propene BDE, because this is a simple bond fission and the interaction of Co^+ with propene should be attractive at long range. This BDE of 1.87 ± 0.07 eV agrees very well with that of Hanratty *et al.*,[27] who measured a 0 K BDE of 1.91 ± 0.22 eV. From our BDE, we calculate that $\Delta_f H°_0(Co^+—\text{propene}) = 248 \pm 2$ kcal/mol.

The observation that the threshold for dissociation of $CoC_3H_6^+$ formed from cyclopropane is about the same value as that for Co^+—propene suggests that this species has rearranged to form the Co^+—propene complex. This is consistent with the observation that virtually all other product channels in Figures 3 and 4 have very similar cross sections. It is possible that the threshold measured for this system is slightly less than that for the propene system because a small amount of a higher energy isomer, presumably the cobaltacyclobutane ion, is present; however, the measured thresholds are the same within experimental error.

The threshold for formation of Co^+ from $CoC_3H_6^+$ formed from cyclobutanone is much lower than in the propene and cyclopropane systems. This suggests that another isomer of this ion is formed in this reaction and is consistent with the results of van Koppen *et al.*,[12] who concluded that the decarbonylation reaction of Co^+ with c-C_4H_6O probably forms the cobaltacyclobutane ion but that it then rearranges to the Co^+—propene isomer. Jacobson and Freiser[10] drew a similar conclusion, because they found that CID and ligand exchange studies with $CoC_3H_6^+$ formed by decarbonylation of cyclobutanone by Co^+ were identical with the results for Co^+—propene ions. In our studies, formation of the metallacycle isomer may be enhanced compared to these studies because of the high-pressure environment in the flow tube. More of this isomer is formed in the cyclobutanone system than in the cyclopropane system because elimination of CO helps to cool the resultant $CoC_3H_6^+$ species and because the conversion of cyclobutanone to cyclopropane and CO is 5.6 kcal/mol endothermic at 0 K (Table 2).

We assume that the threshold of 0.89 ± 0.06 eV corresponds to dissociation of the cobaltacyclobutane ion to form Co^+ + propene rather than Co^+ + cyclopropane because the rearrangement of the metallacycle to the metal−alkene isomer is facile once it has moderate amounts of internal energy. Thus, this threshold indicates that the heat of formation of the cobaltacyclobutane ion is 271 ± 2 kcal/mol (279 ± 2 kcal/mol, assuming dissociation to Co^+ + cyclopropane), in good agreement with the value measured by van Koppen *et al.*,[12] (274 ± 5 kcal/mol). This agreement helps verify the structural assignment.

Finally, we consider the low-energy tails observed on the Co^+ cross sections in all three systems. It is possible that this feature is due to some minor impurity in the ions or neutral reagents or to a small population of excited-state ions, but the reproducibility of this feature from system to system and over the course of several independent data runs taken over the course of 1 year belies such suggestions. The feature has a small cross section, about 0.02 Å^2 in all three systems (Figures 3−5), and is therefore hard to model accurately, but the thresholds are similar in all three systems and the average threshold value is 0.20 ± 0.15 eV. We speculatively assign this feature to a third isomer of $CoC_3H_6^+$, the cobalt π-allyl hydrido ion. This threshold would mean that $\Delta_f H°_0(HCoC_3H_5^+) = 287 \pm 4$ kcal/mol. The assignment is plausible because this isomer is the intermediate required to rearrange between the cobaltacyclobutane ion and Co^+—propene isomers (Scheme 1). This assignment is also consistent with bond additivity assumptions;[28] i.e., if we assume that $D(C_3H_5Co^+—H) \approx D(Co^+—H)$, the $H—Co^+—C_3H_5$ intermediate is calculated to lie 0.23 ± 0.21 eV lower in energy than Co^+ + propene. (Bond additivity also predicts that an alternate possibility, the $H_3C—Co^+—C_2H_3$ isomer, lies 0.14 ± 0.10 eV above the Co^+ + propene asymptote, suggesting that this isomer is a less likely assignment.)

$CoCH_2^+$. The experimental threshold measured for formation of $CoCH_2^+ + C_2H_4$ from $CoC_3H_6^+$ (from cyclopropane) is 1.75 ± 0.20 eV (Table 5). On the basis of the BDE for $CoCH_2^+$ measured above (which leads to $\Delta_f H°_0(CoCH_2^+) = 301.1 \pm 1.6$ kcal/mol) and literature thermochemistry in (Table 2), this threshold yields $\Delta_f H°_0(c\text{-}CoC_3H_6^+) = 275 \pm 5$ kcal/mol, consistent with the value 271 ± 2 kcal/mol derived above (which corresponds to a threshold of 1.94 ± 0.06 eV). In contrast, the experimental threshold for formation of $CoCH_2^+ + C_2H_4$ from $CoC_3H_6^+$ (from cyclobutanone) is 1.49 ± 0.14 eV (Table 5), which leads to $\Delta_f H°_0(CoC_3H_6^+)$

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(27) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; van Koppen, P. A. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1988**, *110*, 1.

(28) More sophisticated estimates can be made that consider promotion energies associated with making two covalent bonds to Co^+. Our estimates using such methods yield results very similar to those given here, because the promotion energy for two bonds is just about twice that for a single bond.[24]

= 281 ± 4 kcal/mol. (This analysis models the cross section over the entire energy range studied but does not accurately reproduce the data in the threshold region.) There are two possible explanations for this result. First, in contrast to the assumption made above, c-$CoC_3H_6^+$ dissociates to Co^+ + cyclopropane, meaning that $\Delta_fH^\circ_0$(c-$CoC_3H_6^+$) = 279 ± 2 kcal/mol, consistent with the $CoCH_2^+$ thresholds measured in both the cyclopropane and cyclobutanone systems within the fairly large experimental errors. Second, the threshold for $CoCH_2^+$ observed in the cyclobutanone system corresponds to dissociation of the cobalt π-allyl hydrido ion ($\Delta_fH^\circ_0(HCoC_3H_5^+)$ = 287 ± 4 kcal/mol). Thus, the $CoCH_2^+$ product cross section is the superposition of dissociation from three separate isomers of $CoC_3H_6^+$: cobaltacyclobutane ion, Co^+—propene, and the cobalt π-allyl hydrido complex ion.

This latter possibility can be checked by determining whether the $CoCH_2^+$ cross section can be accurately modeled if the presence of all three isomers is considered. This is done by taking the thresholds to form the $CoCH_2^+$ product from each of the three isomers and modeling representative cross sections. For the Co^+—propene isomer, we use the cross section from the $CoC_3H_6^+$ (from propene) system with a measured threshold of 5.03 eV (Table 5) and scale it by 40% (a percentage determined below). For the purported cobalt π-allyl hydrido isomer, the $CoCH_2^+$ cross section is analyzed at low energies, below the 1.94-eV threshold expected for $CoCH_2^+$ production from the cobaltacyclobutane isomer. This yields a threshold of about 1.1 ± 0.1 eV, corresponding to $\Delta_fH^\circ_0(CoC_3H_6^+) \approx 290 \pm 2$ kcal/mol, consistent with the heat of formation for this isomer determined above, 287 ± 4 kcal/mol. The remaining part of the cross section can be modeled by eq 1 with a threshold of 1.94 eV, corresponding to $\Delta_fH^\circ_0$(c-$CoC_3H_6^+$) = 271 kcal/mol. This composite reproduction of the data is shown in Figure 7, along with reproductions of the $CoCH_2^+$ cross sections in the other two systems. These results demonstrate the plausibility of contributions from three isomers.

$CoC_3H_6^+$ Potential Energy Surface. On the basis of these experimental results, we are able to construct a potential energy surface (PES) for the Co + $C_3H_6^+$ reaction system (Figure 8). The energies of all species shown in this diagram are determined experimentally. The height of the barrier that separates the Co^+—propene and cobaltacyclobutane ion intermediates cannot be determined conclusively from experimental results. The height of this barrier must be lower than the Co^+ + cyclobutanone − CO (0.11 ± 0.09 eV relative to Co^+ + propene) energy, because Jacobson and Freiser[10] observed that $CoC_3H_6^+$ formed in the reaction of Co^+ + cyclobutanone rearranged to the Co^+—propene structure. The observation that $CoCH_2^+$ + ethene is formed in the bimolecular reaction of Co^+ + propene suggests that the barrier is lower than the Co^+ + propene energy (presuming that this product channel proceeds via the metallacycle intermediate as shown in Scheme 1). Clearly, the barrier cannot lie below the energy of the c-$CoC_3H_6^+$ intermediate, otherwise this isomer could not be produced.

The observation of thresholds for the exothermic $CoC_2H_2^+$ + CH_4 product channels in the two bimolecular systems demonstrates that there is a barrier along the potential energy surface leading to this product. The observation that the measured barrier height in the two systems differs by the heat of formation of the reactants indicates that the barrier is the same in both systems. This barrier could correspond to the activation of the C—C bond to form the CH_3—Co^+—C_2H_3 intermediate, to the β-H transfer step that forms $(CH_3)(H)Co^+(C_2H_2)$, to the reductive elimination of methane to form products, or to some other point along the surface. To estimate which of these might be most important, we use bond additivity arguments to assess the relative energies of these intermediates. As noted above, the

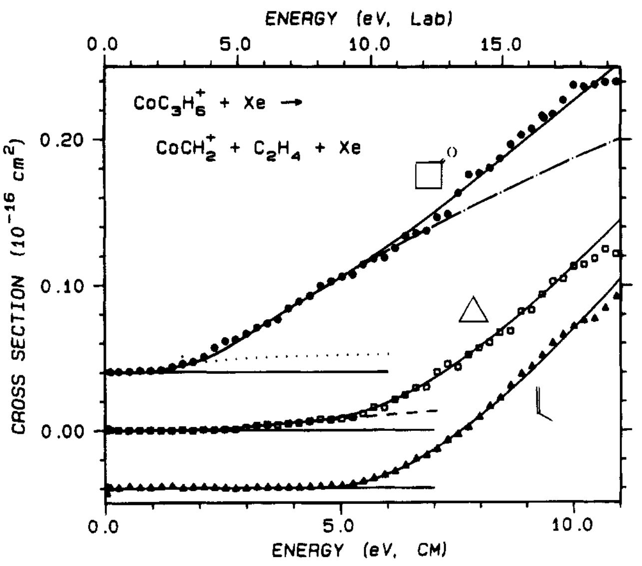

Figure 7. $CoCH_2^+$ product cross sections from the reaction of $CoC_3H_6^+$ with xenon as a function of relative energy (lower x axis) and laboratory energy (upper x axis). Data are shown for $CoC_3H_6^+$ made by adding cyclobutanone (solid circles), cyclopropane (open squares), and propene (solid triangles) to the flow tube. The cyclobutanone and propene data have been offset from zero for clarity. The lines show the models of eq 1 with the parameters listed in Table 5 after convolution over the experimental kinetic energy distributions. The line through the propene data represents the cross section corresponding to dissociation of 100% Co^+—propene isomer (E_0 = 5.03 eV). The line through the cyclopropane data represents 15% of the metallacycle ion isomer cross section (E_0 = 1.94 eV, dashed line) plus 85% of the Co^+—propene isomer cross section. The line through the cyclobutanone data represents a small contribution from a third isomer (E_0 = 1.1 eV, dotted line), plus 60% of the metallacycle ion isomer cross section (dash–dot line), plus 40% of the Co^+—propene isomer cross section.

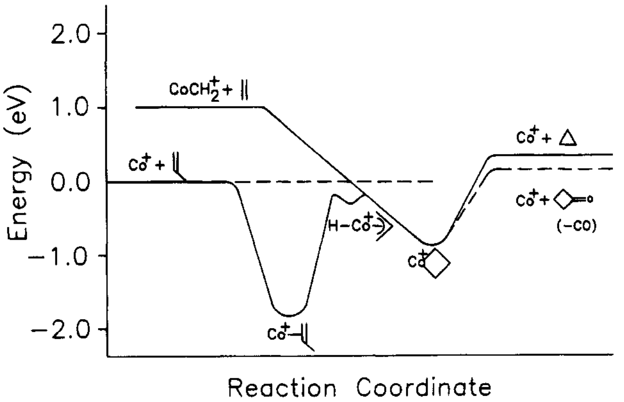

Figure 8. Potential energy surface for the $[CoC_3H_6]^+$ system. The location of Co^+ + cyclobutanone is placed on the potential energy surface after subtracting $\Delta_fH^\circ_0$(CO).

$CH_3—Co^+—C_2H_3$ intermediate is estimated to lie 0.14 ± 0.10 eV above the energy of the Co^+ + propene reactants. To estimate $D(Co^+—C_2H_2)$, we compare theoretical values for $D_e(Co^+—C_2H_2) = 1.44$ eV[26] and $D_e(Co^+—C_2H_4) = 1.58$ eV[29] with the experimental value of $D_0(Co^+—C_2H_4) = 1.86 \pm 0.07$ eV[30] (Table 3) to yield $D_0(Co^+—C_2H_2) \approx 1.72$ eV. By using this value in a bond additivity scheme, we find that the $(CH_3)(H)Co^+(C_2H_2)$ intermediate has the same energy as these reactants within about 0.10 eV and the $CoC_2H_2^+ + CH_4$ products lie ~0.40 eV below. These estimates do not point definitively to one particular step as rate limiting, but we note that the measured barrier to reaction 15 of 1.00 ± 0.12 eV is probably consistent with the C—C bond activation step, as estimated from recent studies of the related Co^+ and Fe^+ + propane system.[15,31–33]

Discussion

Bimolecular Reactions. Analysis of the Co^+ + cyclopropane and Co^+ + propene reactions shows several differences. The most evident difference is the $CoCH_2^+$ product which is efficiently produced in the Co^+ + cyclopropane system and not the Co^+ + propene system. The $CoCH_2^+$ cross section is about 2 orders of magnitude smaller for the propene reaction when compared to the cyclopropane reaction. One explanation is that $CoCH_2^+$ can be easily formed from the cobaltacyclobutane structure intermediate (Scheme 1). For the propene reaction, several rearrangements must first take place, making production of the $CoCH_2^+$ product inefficient.

The $CoC_2H_4^+$ product has a maximum cross section magnitude of about 0.4 Å^2 in the cyclopropane reaction. In the propene reaction, this same product has a magnitude at least 1 order of magnitude smaller. This observation is consistent with Scheme 1, which shows the product coming from the cobaltacyclobutane intermediate.

Conversely, the amount of $CoCH_3^+$ formed is larger (by a factor of about 4) in the propene reaction than in the cyclopropane reaction. This again seems consistent with Scheme 1, where the pathway to form this product from propene is less involved than that from cyclopropane. However, the cross sections for $CoC_2H_3^+$ and $CoC_2H_2^+$ are comparable in the two systems, even though they come from the same postulated intermediate as $CoCH_3^+$. Overall, these results appear to indicate that it is much easier for the intermediates formed from Co^+ + cyclopropane to rearrange to those formed from Co^+ + propene than is the reverse. This is consistent with the observations of previous workers[10,12] that the cobaltacyclobutane ion appears to rapidly rearrange to the Co^+—propene isomer.

Bimolecular versus Threshold Collisional Activation Reactions. Propene. We would expect the bimolecular reaction of Co^+ + propene (Figure 2) and the threshold collisional activation (TCA) of Co^+—propene (Figure 3) to yield similar results, because these reactions take place on the same global potential energy surface (PES). Of course, the product thresholds for the Co^+—propene TCA reaction must be shifted up in energy by at least $D(Co^+—\text{propene})$. They are observed to shift more than this, as can be seen from a comparison of the thermodynamic and apparent thresholds. This is because a wide distribution of energies (ranging from 0 for a large impact parameter to the total relative kinetic energy for an impact parameter of 0) is deposited in the Co^+—propene complex by the collision with Xe. Thus, the *average* energy deposited in the TCA complex is considerably less than the indicated collision energy and the thresholds exhibit a kinetic shift. If sufficient signal intensity were available, it should be possible to observe these products at their thermodynamic thresholds, but this is hindered by the competition with simple CID to form Co^+ + propene + Xe and ligand exchange to form $CoXe^+$ + propene. Thus, the products observed in Figure 2 have cross sections that are about a factor of 5 smaller in the TCA experiment than in the bimolecular experiment. These products, which involve C—C and C—H bond activation processes, are kinetically much less likely than the cleavage of an intact propene molecule. The predominance of kinetically favored products is also indicated by the observation that the other products in Figure 3 are those involving direct cleavage of a C—H (CoH^+ and $C_3H_5^+$) or C—C bond ($CoC_2H_3^+$ and $CoCH_3^+$), rather than those involving more complicated rearrangements, such as $CoC_2H_2^+$ (which is observed but has a cross section of only 0.01 Å^2) or $CoC_3H_4^+$.

Cyclopropane. The observation that TCA of $CoC_3H_6^+$ generated from cyclopropane (Figure 4) and that generated from propene (Figure 3) are nearly identical confirms that the adduct formed by condensation of Co^+ with cyclopropane rapidly rearranges to the Co^+—propene isomer. Thus, the bimolecular results of Figure 1 and the TCA results of Figure 4 do not correspond. The only difference between the results of Figures 3 and 4 is the tail on the $CoCH_2^+$ cross section, which has a threshold that corresponds to the cobaltacyclobutane ion isomer. Thus, a small percentage (estimated below) of this $CoC_3H_6^+$ beam appears to have retained the metallacycle structure. No other products exhibit significant changes, because the $CoCH_2^+$ product is the most sensitive to the metallacycle intermediate, consistent with the differences between Figures 1 and 2.

Isomer Percentages. A comparison of the CoH^+ and $CoC_2H_3^+$ product cross sections in the TCA of $CoC_3H_6^+$ formed from all three precursors shows that they all have the same energy dependence. The magnitudes are within the experimental error of 20% for the propene and cyclopropane precursors (an average ratio of 1.0:0.85 is measured), but the magnitude of the $CoC_2H_3^+$ cross section in the cyclobutanone system is only 40% as large as those in the other two systems. The relative error in these cross-section magnitudes is estimated as 10%. On the basis of Scheme 1, the $CoC_2H_3^+$ product is believed to be characteristic of the Co^+—propene isomer. This is supported by the observation that $FeC_2H_3^+$ was observed as a product in the TCA of Fe^+—propene but not that of the ferracyclobutane ion.[1] Thus, these results suggest that the Co^+—propene isomer comprises 100%, 85 ± 10%, and 40 ± 10% of the $CoC_3H_6^+$ beams formed from the propene, cyclopropane, and cyclobutanone precursors, respectively.

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This estimate of the isomer percentages can be checked by a comparison of the $CoCH_2^+$ cross sections in the three TCA experiments. At high energies (above ~5 eV), these cross sections are the same within experimental error in the propene and cyclopropane systems (Figure 7). At low energies (below ~5 eV), the cross section in the propene system is absent, and that in the cyclopropane system is about 1 order of magnitude smaller than in the cyclobutanone system. As indicated by the thermochemistry, this low-energy $CoCH_2^+$ cross section can be attributed primarily to the cobaltacyclobutane ion isomer. An estimate of the absolute cross section for $CoCH_2^+$ coming from this isomer is obtained by subtracting 40% of the $CoCH_2^+$ cross section obtained in the propene system (thereby accounting for contributions arising from the Co^+—propene isomer) from the $CoCH_2^+$ cross section in the cyclobutanone system and then scaling to 100% by multiplying the remainder by 1.67 (=100%/60%). When 15% of this cross section and 85% of the $CoCH_2^+$ cross section arising from the Co^+—propene isomer are added together, the $CoCH_2^+$ cross section in the Co^+—cyclopropane system is reproduced (Figure 7). Thus, the final estimates of the Co^+—propene and cobaltacyclobutane ion isomer percentages are 100:0, 85:15, and 40:60 with errors of about 10% for the propene, cyclopropane, and cyclobutanone precursors, respectively. Although these percentages represent the most reproducible results obtained, we should also note that the exact percentages of the two isomers were observed to depend on the specific conditions in the flow tube. The presence of a third isomer is also possible, as noted above, but on the basis of the size of the features in the Co^+ cross sections attributable to this isomer, it does not appear to constitute more than 1% of the ion beams and, therefore, was not taken into account.

It makes sense that the cyclobutanone precursor yields the highest amount of the metallacycle, because the CO molecule can carry away excess energy, thereby stabilizing this intermediate. In contrast, most of the $CoC_3H_6^+$ formed by condensation of Co^+ with cyclopropane rearranges because this intermediate has substantially more internal energy, as is evident from the potential energy surfaces shown in Figure 8. The observation of the metallacycle ion in the present experiments is in contrast with the failure of Jacobson and Freiser[10] to observe evidence of this intermediate. This difference is due to the high-pressure conditions in our flow-tube source, which provide three-body collisions that stabilize the metallacycle. In the absence of these collisions, rearrangement of the metallacycle to the metal−propene ion is driven by the relative stability of the two isomers.

Finally, we use these isomer percentages to reevaluate the threshold for formation of Co^+ product by TCA of the cobaltacyclobutane ion. This was achieved by scaling the Co^+ cross section for Co^+—propene (Figure 3) by 40% and subtracting it from the Co^+ cross section in the cyclobutanone TCA experiment. The resultant cross section was then analyzed with eq 1 to yield an optimum threshold of 0.93 ± 0.07 eV (Table 5), nearly the same as the value obtained before correction (0.89 ± 0.06 eV). If we assume that the metallacycle dissociates to Co^+ + propene, this revised threshold indicates $\Delta_f H^\circ_0(\text{c-CoC}_3\text{H}_6^+) = 270 \pm 2$ kcal/mol.

$FeC_3H_6^+$ Metallacycle and Metal−Alkene Isomer Systems. In contrast to the present results for $CoC_3H_6^+$, formation of $FeC_3H_6^+$ by condensation of Fe^+ with propene and cyclopropane yields very different results, consistent with formation of the Fe^+—propene and ferracyclobutane ions, respectively.[1] The distinct differences between these two neighbors in the periodic table suggest that the barrier between the two isomers is much higher in the iron case than in the cobalt case, as also concluded by van Koppen *et al.*[12] A complication in the iron case involves the fact that the $Fe^+(a^4F,3d^7)$ state which is analogous to the $Co^+(a^3F,3d^8)$ ground state lies above the $Fe^+(a^6D,4s^13d^6)$ ground state.[34] In the cobalt case, the ground states of $CoCH_2^+$,[25] Co^+—propene (presumed to be the same as Co^+—ethene),[29] and c-$CoC_3H_6^+$ (if the Co−C bonds are both covalent) all have triplet spin. Thus, rearrangements among the various $[CoC_3H_6]^+$ reactants, products, and intermediates are all spin-allowed, as indicated in Figure 8. In the iron case, the ground state of $FeCH_2^+$ is $^4B_1$,[25] the ground state of Fe^+—propene should be quartet,[29] and the c-$FeC_3H_6^+$ metallacycle is likely to have a quartet ground state if both Fe−C bonds are covalent. Thus, rearrangements among the various $[FeC_3H_6]^+$ species are spin-allowed on the quartet surface, but this must cross the surfaces evolving from the ground-state $Fe^+(a^6D)$ + propene and cyclopropane asymptotes. It seems likely that these surface crossings also influence the observed dynamics, because Schultz and Armentrout have noted that both $Fe^+(a^6D)$ and $Fe^+(a^4F)$ react with cyclopropane to form $FeCH_2^+ + C_2H_4$.[1]

Conclusions

We have studied two isomers of $CoC_3H_6^+$ by using guided-ion-beam mass spectrometry to examine the bimolecular reactions of Co^+ with propene and cyclopropane. Particular attention was paid to generation of electronically cold Co^+ ions in these studies. In addition, $CoC_3H_6^+$ species are formed by condensation of Co^+ with propene or cyclopropane and decarbonylation of cyclobutanone by Co^+ in a high-pressure flow-tube source. These adducts are then probed by using threshold collisional activation. All results can be interpreted in terms of two isomers, Co^+—propene and the cobaltacyclobutane ion, and possibly a third, $H{-}Co^+{-}C_3H_5$, which are formed in different ratios depending on the precursor and source conditions. The results indicate that the less stable metallacycle can readily rearrange to the more stable metal−alkene isomer, in contrast to comparable results for $FeC_3H_6^+$ isomers.[1] The thermochemistry derived for these two isomers, heats of formation of 270 ± 2 and 248 ± 2 kcal/mol, respectively, is in good agreement with less precise values obtained previously by very different methods.[12] The putative cobalt π-allyl hydrido ion is estimated to have a heat of formation of 287 ± 4 kcal/mol. Bond energies for $Co^+{-}C_2H_3$, $Co^+{-}C_3H_4$, and $Co^+{-}C_3H_5$ and a refined value for $Co^+{-}CH_2$ are also obtained.

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