

to give the following discrepancy indices:

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.165$$

$$R_2 = [\sum w(|F_o| - |F_c|) / \sum w|F_o|]^2]^{1/2} = 0.232$$

The function minimized in least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$ , where the weighting factor,  $w$ , equals  $4F_o^2 / \sigma(F_o)^2$ . A value of 0.07 was used for the parameter  $p$  in the weighting function.<sup>26</sup> The atomic scattering factors used were those of Cromer and Waber.<sup>27</sup> Anomalous dispersion effects<sup>28</sup> were included in the calculated scattering factors. A difference Fourier synthesis at this point revealed the positions of 24 nonhydrogen atoms belonging to 6 independent ligands. Refinement of the positional and isotropic thermal parameters of these atoms, followed by a second difference Fourier synthesis, revealed the positions of the atoms of the seventh ligand. The positional and isotropic thermal parameters of the 30 nonhydrogen atoms were refined to yield discrepancy indices  $R_1 = 0.097$  and  $R_2 = 0.117$ . At this point, an absorption correction was applied to the data since  $\mu = 83.6 \text{ cm}^{-1}$ . The maximum, minimum, and average transmission coefficients were 0.351, 0.181, 0.302, respectively. Refinement was then continued employing isotropic thermal parameters, to yield  $R_1 = 0.057$  and  $R_2 = 0.075$ .

(26) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organomet. Chem.*, **50**, 227 (1973).

(27) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.3.1.

(28) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

Examination of a difference Fourier map suggested that the isopropyl group attached to O(4) was disordered. A twofold disorder about the O(4)-C(41) bond was indicated. It was assumed that four methyl groups (C(42), C(43), C(44), C(45)), each having an occupation number of 0.5, were bonded to C(41). Inspection of the C(41) to methyl bond lengths indicated that C(41) might itself be slightly disordered. However, since the displacement was slight ( $\sim 0.2 \text{ \AA}$ ), it was ignored. All atoms were now refined to convergence, utilizing anisotropic thermal parameters for the tungsten and oxygen atoms and isotropic thermal parameters for the carbon atoms. The residuals at this point were  $R_1 = 0.037$  and  $R_2 = 0.052$ , and the esd of an observation of unit weight was 1.25.

Since extra crystallographic considerations had led us to consider the possible presence of hydrogen atoms in bridging positions, we now made an effort to find and refine them. A weak peak lying near the "empty" bridging position between W(1) and W(2) was introduced as a hydrogen atom, and refinement was continued to a new convergence. The hydrogen atom behaved quite well in refinement, and the final figures of merit were  $R_1 = 0.033$ ,  $R_2 = 0.045$ , and esd = 1.10, and no parameter shifted by more than 0.1 times its esd in the last cycle.

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**Supplementary Material Available:** A listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

## Ion Beam Studies of the Reactions of Atomic Cobalt Ions with Alkanes: Determination of Metal-Hydrogen and Metal-Carbon Bond Energies and an Examination of the Mechanism by which Transition Metals Cleave Carbon-Carbon Bonds

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**Abstract:** An ion beam apparatus is employed to study the reactions of singly charged cobalt positive ions with hydrogen and 17 alkanes. Reaction cross sections and product distributions as a function of kinetic energy are determined. Exothermic carbon-carbon bond cleavage reactions are observed for all alkanes but methane and ethane. A mechanism involving oxidative addition of C-C and C-H bonds to cobalt as a first step is demonstrated to account for all major reactions at all energies. Interpretation of several endothermic processes allows the extraction of thermochemical data. The bond dissociation energies obtained are  $D^\circ(\text{Co}^+-\text{H}) = 52 \pm 4 \text{ kcal/mol}$ ,  $D^\circ(\text{Co}-\text{H}) = 39 \pm 6 \text{ kcal/mol}$ ,  $D^\circ(\text{Co}^+-\text{CH}_3) = 61 \pm 4 \text{ kcal/mol}$ , and  $D^\circ(\text{Co}-\text{CH}_3) = 41 \pm 10 \text{ kcal/mol}$ .

### Introduction

A recent article<sup>1</sup> pointed out that the "fuzzy interface between surface chemistry, heterogeneous catalysis, and organometallic chemistry" is the transition metal-organic fragment bond. Despite the importance of such information, little is known about the thermodynamics of such bonds.<sup>2</sup> Ab initio calculations<sup>1,3</sup> are one means of obtaining such information, but experimental numbers are needed. Gas-phase studies using ion cyclotron resonance spectroscopy<sup>4-6</sup> have yielded thermochemical data for transition

metal-carbon bonds. The present study utilizes a different technique for determining gas-phase metal-hydrogen and metal-carbon bond energies which has been presented in brief previously.<sup>7</sup> With use of an ion beam apparatus, the reactions of atomic cobalt ions with alkanes ranging in complexity from

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(5) (a) J. Allison and D. P. Ridge, *J. Am. Chem. Soc.*, **98**, 7445 (1976); (b) J. Allison, R. B. Freas, and D. P. Ridge, *ibid.*, **101**, 1332 (1979); (c) J. Allison and D. P. Ridge, *ibid.*, **101**, 4998 (1979).

(6) A. E. Stevens and J. L. Beauchamp, *J. Am. Chem. Soc.*, **100**, 2584 (1978); **101**, 245, 6449 (1979).

(7) P. B. Armentrout and J. L. Beauchamp, *J. Am. Chem. Soc.*, **102**, 1736 (1980).

(1) H. F. Schaefer, *Acc. Chem. Res.*, **10**, 287 (1977).

(2) J. A. Connor, *Top. Curr. Chem.*, **71**, 71 (1977).

(3) A. K. Rappé and W. A. Goddard III, *J. Am. Chem. Soc.*, **99**, 3966 (1977); T. H. Upton and W. A. Goddard III, *ibid.*, **100**, 321, 5659 (1978).

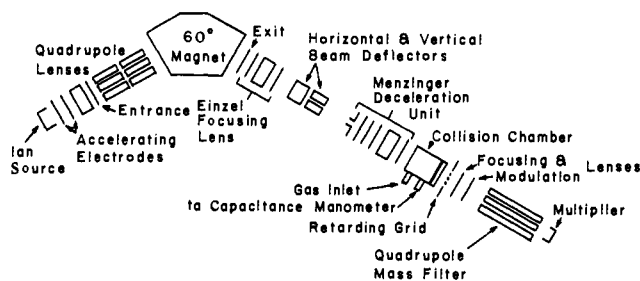


Figure 1. Schematic drawing of the ion beam apparatus.

methane to branched octanes have been examined. By varying the kinetic energy at which the  $\text{Co}^+$  interacts with the alkanes, it is possible to probe the potential energy surface of these systems. This allows a variety of thermochemical information to be derived.

In addition, the general reactivity of alkanes with  $\text{Co}^+$  is assessed. For all alkanes larger than ethane, exothermic cleavage of carbon-carbon bonds is observed. Several recent studies have shown that metal atoms,<sup>8,9</sup> small metal clusters,<sup>9,10</sup> and atomic metal ions<sup>5,7</sup> cleave hydrocarbons. We provide direct evidence that such reactions occur by oxidative addition of carbon-carbon bonds to the metal. Facile  $\beta$ -hydrogen abstraction by the metal and reductive elimination of hydrogen or a hydrocarbon complete the general mechanism. The reactions of  $\text{Co}^+$  with 17 alkanes are shown to be consistent with such a proposal.

### Experimental Section

The ion beam apparatus, described in detail elsewhere,<sup>11,12</sup> is shown schematically in Figure 1. Ions from a surface ionization source are mass analyzed by using a  $60^\circ$  sector magnet which provides unit mass resolution to greater than  $m/z$  100. This mass-selected beam is decelerated to a selected energy and focused into a collision chamber containing the reactant gas. Product ions exit the chamber with the aid of a 0.5-V extraction field.<sup>13</sup> These ions are focused into a quadrupole mass filter and detected by using a Channeltron electron multiplier operated in a pulse-counting mode. Ion signal intensities are corrected for the mass discrimination of the quadrupole mass filter.

The source for cobalt ions is described in detail elsewhere.<sup>11,14</sup> Briefly,  $\text{CoCl}_2$  is evaporated onto a rhenium filament where dissociation and ionization of the resulting Co occurs. This method of ionization minimizes the production of excited metal ion states. It is estimated that at the filament temperature used,  $\sim 2500$  K, 81% of the  $\text{Co}^+$  ions produced are in the  $^3\text{F}$  ground-state manifold and 19% are in the  $^5\text{F}$  excited-state manifold at 0.42 eV. In order to observe the effects of an excited state, its lifetime must exceed about  $10 \mu\text{s}$ , the approximate flight time of the ions. An attempt was made to directly determine the presence of excited ions by using an attenuation technique.<sup>15,16</sup> Only a single component was detected, suggesting that excited states are absent. This assumes that the  $^3\text{F}$  and  $^5\text{F}$  states have different total scattering cross sections for the collision gases used ( $\text{O}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$ ).

The nominal collision energy of the ion beam is taken as the difference in potential between the center of the collision chamber and the center of the filament, the latter being determined by a resistive divider. This collision energy is verified by use of a retarding field energy analyzer.<sup>12</sup> Agreement was always within 0.3 eV. Two other factors which affect the collision energy are the energy distribution of the  $\text{Co}^+$  beam and the thermal motion of the target gas. The former is determined to be 0.7 eV (fwhm) by using the retarding field analyzer. In the present experiments, this spread is sufficiently small compared to the second factor so that it will be disregarded.<sup>17</sup> The effect of the thermal motion of the

Table I. Thermochemistry of Cobalt-Hydrogen and Cobalt-Carbon Bonds Derived in This and Related Studies

R	$D^\circ(\text{Co}^+-\text{R})$ , kcal/mol	IP, eV	$D^\circ(\text{Co}-\text{R})$ , kcal/mol
H	$52 \pm 4^a$	$7.3 \pm 0.1^b$	$39 \pm 6$
$\text{CH}_3$	$61 \pm 4^{a,c}$	$7.0 \pm 0.3^d$	$41 \pm 10$
$\text{CH}_2$	$85 \pm 7^e$		

<sup>a</sup> Calculated as described in text. <sup>b</sup> Reference 41. <sup>c</sup> Comparison of the  $\text{CoCH}_3^+$  product yields to those of other cobalt alkyl ion products suggests that larger alkyls are bonded only a little less strongly than  $\text{CH}_3$  to  $\text{Co}^+$ . <sup>d</sup> Reference 38. <sup>e</sup> Reference 14.

reactant gas in ion beam collision chamber experiments has been discussed in detail elsewhere.<sup>17,18</sup> The energy broadening due to this motion washes out any sharp features in reaction cross sections. For exothermic reactions this has little effect on the observed cross sections and branching ratios. Consequently we report such data without taking this energy distribution into account. For endothermic reactions, the thermal motion obscures the threshold energy for reactions. By convoluting a functional form for the reaction cross section,  $\sigma(E)$ , with the thermal energy distribution, using the method of Chantry,<sup>18</sup> and fitting this new curve to the data, we take specific account of this factor.

The analysis of endothermic reactions to obtain thermochemical data is not a subject without controversy. Our choice for the functional form of the reaction cross section is discussed in detail elsewhere.<sup>14</sup> The form used, eq 1, has three variable parameters:  $\sigma_0$ , an effective cross section;

$$\sigma(E) = \sigma_0[(E - E_0)/E]^n \quad (1)$$

$E_0$ , the energy threshold for reaction (taken equal to the difference in bond energies of the neutral reactant (bond broken) and ionic product (bond formed)); and  $n$ . Equation 1 is expected to apply for energies below the threshold for dissociation of the product ion. This threshold corresponds to the energy of the bond broken in the neutral reactant. Detailed treatments of the effect of dissociation on the observed reaction cross section also have been discussed previously.<sup>14,19</sup>

Reaction cross sections for specific products,  $\sigma_i$ , are obtained by using eq 2 and 3 which relate the total reaction cross section,  $\sigma$ , the number

$$I_0 = (I_0 + \sum I_i) \exp(-n_0 \sigma l) \quad (2)$$

$$\sigma_i = \sigma I_i / \sum I_i \quad (3)$$

density of the target gas,  $n_0$ , and the length of the collision chamber,  $l$  (5 mm), to the transmitted reactant ion beam intensity,  $I_0$ , and the sum of the product ion intensities,  $\sum I_i$ . The pressure of the target gas, measured by using an MKS Baratron Model 90H1 capacitance manometer, is kept low ( $< 2 \times 10^{-3}$  torr) to minimize attenuation of the beam and ensure that reactions are the result of only a single bimolecular collision. However, it was found with the heavier alkanes that total cross sections were not accurately reproducible and were generally much higher than is predicted by using the Langevin-Gioumousis-Stevenson model for ion-molecule reactions.<sup>20</sup> We attribute this effect to substantial loss of elastically scattered  $\text{Co}^+$  from the reactant beam. Relative cross sections of products (branching ratios) were quite reproducible, and the results for the larger alkanes are reported in this manner.

It is important to point out that neutral products are not detected in these experiments. However, except where noted below, the identity of these products can usually be inferred without ambiguity. In addition, these experiments provide no direct structural information about the ionic products. Thermochemical arguments can often distinguish possibilities for isomeric structures.

### Results and Discussion

A wide variety of reactions result from a single bimolecular collision of  $\text{Co}^+$  with alkanes. The particular products observed are dependent on the kinetic energy of the interaction as well as the structure of the alkane. In the following section, the reactions of cobalt ions with hydrogen, methane, and ethane are examined first. Detailed analyses of these reactions, all endothermic, allow a determination of important thermochemical data, summarized in Table I. Next, the reactions of  $\text{Co}^+$  with propane, butane, 2-methylpropane, and 2,2-dimethylpropane are presented. Results

(8) R. J. Remick, T. A. Asunta, and P. S. Skell, *J. Am. Chem. Soc.*, **101**, 1320 (1979).

(9) P. H. Barrett, M. Pasternak, and R. G. Pearson, *J. Am. Chem. Soc.*, **101**, 222 (1979).

(10) S. C. Davis and K. J. Klabunde, *J. Am. Chem. Soc.*, **100**, 5973 (1978).

(11) P. B. Armentrout, R. V. Hodges, and J. L. Beauchamp, *J. Chem. Phys.*, **66**, 4683 (1977).

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(13) The chamber is designed to allow efficient extraction of low energy ions. H. W. Werner, *Int. J. Mass Spectrom. Ion Phys.*, **14**, 189 (1974).

(14) P. B. Armentrout and J. L. Beauchamp, *J. Chem. Phys.*, submitted for publication.

(15) B. R. Turner, J. A. Rutherford, and D. M. J. Compton, *J. Chem. Phys.*, **48**, 1602 (1968).

(16) R. J. Cotter and W. S. Koski, *J. Chem. Phys.*, **59**, 784 (1973).

(17) C. Lifshitz, R. L. C. Wu, T. O. Tiernan, and D. T. Terwilliger, *J. Chem. Phys.*, **68**, 247 (1978).

(18) P. J. Chantry, *J. Chem. Phys.*, **55**, 2746 (1971).

(19) (a) P. B. Armentrout and J. L. Beauchamp, *J. Chem. Phys.*, **48**, 315 (1980); (b) P. B. Armentrout and J. L. Beauchamp, *ibid.*, **50**, 37 (1980).

(20) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

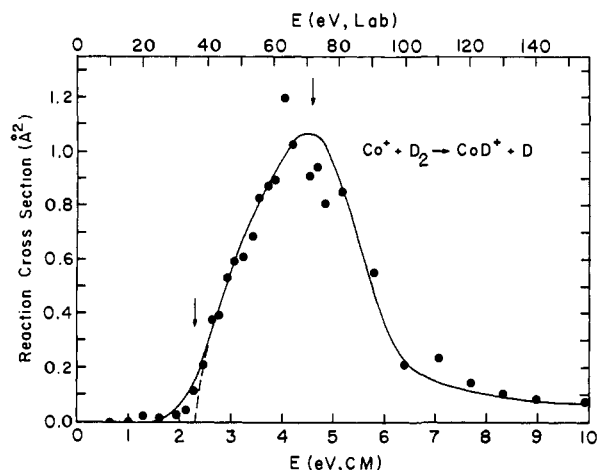


Figure 2. Variation in experimental cross section for reaction 4 as a function of kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale). The solid line is the fit to the data described in the text. The dashed line is the fit in the threshold region before convolution. Arrows mark the threshold energy at 2.3 eV, and the bond energy of  $D_2$  at 4.6 eV.

for these systems establish a general reaction mechanism which explains the processes observed not only for these alkanes but also for all hydrocarbons examined. Finally, results for larger alkanes up to the  $C_8$  species are summarized and discussed.

**Reaction of  $Co^+$  with  $D_2$ .** Cobalt ions react with  $D_2$ , used to facilitate mass resolution, to form  $CoD^+$  as indicated in eq 4.



Cross section data are presented in Figure 2. Previous studies of such metal ion-hydrogen systems<sup>11,19</sup> have been interpreted by using eq 1 with  $n = 1$ . The fit to the data uses eq 1 with  $\sigma_0 = 2.3 \text{ \AA}^2$  and  $E_0 = 2.3 \pm 0.1 \text{ eV}$  and is shown in Figure 2 both unconvoluted and convoluted as discussed above. The decreasing cross section at high energies is due to  $CoD^+$  dissociation which has a thermodynamic threshold at  $D^0(D_2) = 4.60 \text{ eV}$ .<sup>21</sup> The fit shown in Figure 2 above this energy uses an analysis discussed in detail elsewhere.<sup>19</sup>

From the reaction threshold,  $E_0 = 2.3 \pm 0.1 \text{ eV}$ , and the  $D_2$  bond energy, a value for  $D^0(Co^+-D)$  of  $2.3 \pm 0.14 \text{ eV}$  is determined. Making a zero-point energy correction of 0.05 eV,<sup>22</sup>  $D^0(Co^+-H) = 2.25 \pm 0.17 \text{ eV}$  ( $52 \pm 4 \text{ kcal/mol}$ ) is obtained.<sup>23</sup> The proton affinity of the cobalt atom,  $PA(Co)$ , can be calculated by using eq 5, in which  $IP(x)$  is the ionization potential of species

$$PA(Co) = D^0(Co^+-H) + IP(H) - IP(Co) \quad (5)$$

x. The value derived<sup>24</sup> ( $184 \pm 4 \text{ kcal/mol}$ ) is similar to the proton affinities of Ni ( $180 \pm 3 \text{ kcal/mol}$ ),<sup>19b</sup> Fe ( $< 203 \text{ kcal/mol}$ ),<sup>5c</sup> and Zn ( $\sim 164 \text{ kcal/mol}$ )<sup>25</sup> but substantially less than those of such strong atomic bases as Ba ( $250 \pm 3 \text{ kcal/mol}$ )<sup>19a</sup> and U ( $238 \pm 4 \text{ kcal/mol}$ ).<sup>11</sup>

**Reaction of  $Co^+$  with Methane.** The primary reaction of  $Co^+$  with  $CH_4$  is endothermic hydrogen abstraction (process 6). The

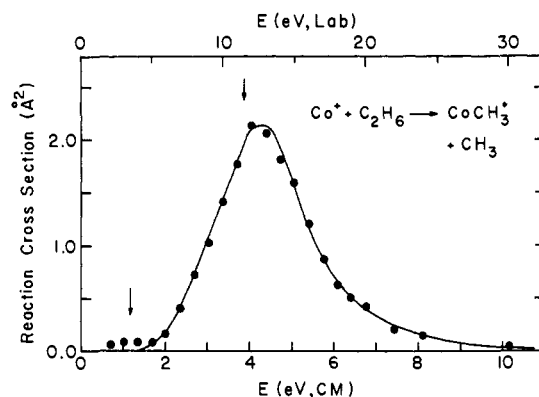
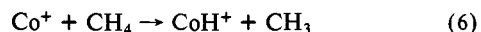
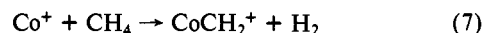
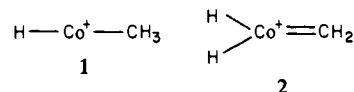


Figure 3. Variation in experimental cross section for reaction 9 as a function of kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale). Arrows mark the threshold energy at 1.25 eV and the carbon-carbon bond energy of ethane at 3.9 eV. The solid line is the fit to the data described in the text.

quality of the data is insufficient to accurately analyze for an energy threshold. Two other products,  $CoCH_2^+$  and  $CoCH_3^+$ , are also observed in this system. The cross sections for both ions peak at about 4 eV, but even at this energy, they account for less than 10% of the reaction products. The energetic requirements are such that the  $CoCH_2^+$  product must be formed in reaction 7, calculated to be 1.1 eV endothermic<sup>14,26</sup> (Table I). Formation of two H atoms as the neutral products would require an additional 4.5 eV.

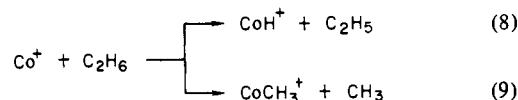


We postulate that both  $CoCH_2^+$  and  $CoCH_3^+$  are formed via intermediate **1**, produced by oxidative addition of a C-H bond



to  $Co^+$ . The lowest energy reaction of **1**, other than proceeding back to reactants, is rearrangement by  $\alpha$ -hydrogen migration from carbon to cobalt,<sup>27</sup> yielding **2**, which can then reductively eliminate  $H_2$ . Alternatively, **1** can decompose directly by breaking the cobalt-hydrogen bond to give  $CoCH_3^+$  or by breaking the cobalt-carbon bond to yield  $CoH^+$ . Since the  $Co^+-CH_3$  bond is stronger than the  $Co-H$  bond (see below), the former product is thermodynamically preferred. Yet,  $CoH^+$  is the predominant product at all energies examined, suggesting as one explanation that  $CoH^+$  is formed by direct hydrogen abstraction rather than through **1**. Alternatively, frequency factors for  $CoH^+$  formation may be substantially greater than those for  $CoCH_3^+$  formation. However, an accurate appraisal of such frequency factors in the absence of reliable geometries is difficult at best and has not been attempted here.

**Reaction of  $Co^+$  with Ethane.** Processes 8 and 9, both endo-



thermic, are the two major reactions observed in the interaction of cobalt ions with ethane. The  $CoH^+$  product has a threshold which agrees qualitatively with the thermodynamics discussed above and a cross section of comparable magnitude to that of the  $CoCH_3^+$  product. The data for reaction 9, shown in Figure 3, have been analyzed by using eq 1. The fit obtained (Figure 3) uses  $\sigma_0 = 14.0 \text{ \AA}^2$ ,  $n = 5$ , and  $E_0 = 1.25 \pm 0.1 \text{ eV}$ . Above the

(21) B. de B. Darwent, *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)*, NSRDS-NBS 31 (1970).

(22) This estimate is based on an estimated frequency for  $CoH^+$  of  $2000 \text{ cm}^{-1}$ .

(23) For comparison, electron impact ionization studies of the molecules,  $HCo(CO)_x(PF_3)_{4-x}$ , where  $x = 0-4$ , yield values for  $D^0(Co^+-H)$  ranging from 1.8 to 3.3 eV with a mean of 2.6 eV. F. E. Saalfeld, M. V. McDowell, S. K. Gondal, and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **90**, 3684 (1968).

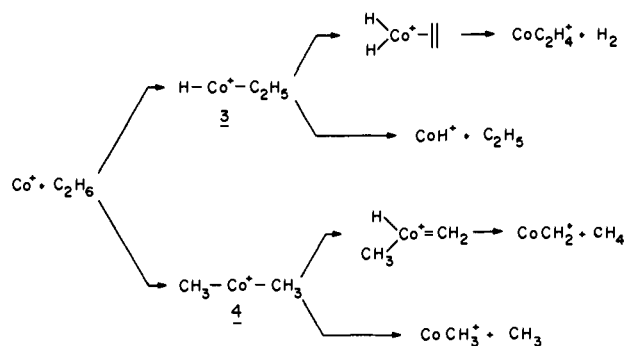
(24) Supplementary thermochemical data for ions and ionization potentials are taken from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, **6** (1977).

(25) Calculated by using  $D^0(Zn^+-H) = 2.5 \text{ eV}$ . G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand, New York, 1950.

(26) Supplementary thermochemical data for hydrocarbons are taken from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, 1970.

(27) Such a process involving cobalt has been observed by L. S. Pu and A. Yamamoto, *J. Chem. Soc., Chem. Commun.*, **9** (1974).

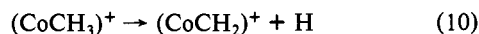
Scheme I



carbon-carbon bond dissociation energy of ethane (3.90 eV),<sup>26</sup> where dissociation of the  $\text{CoCH}_3^+$  product may occur, the fit uses an analysis discussed in detail elsewhere.<sup>14</sup>

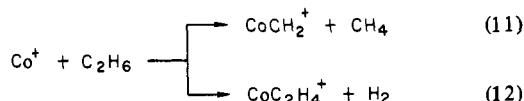
The  $\text{Co}^+-\text{CH}_3$  bond energy, found to be  $2.65 \pm 0.17$  eV ( $61 \pm 4$  kcal/mol), agrees well with the range of values determined by Allison and Ridge (56–69 kcal/mol).<sup>5c</sup> The observation that  $D^0(\text{Co}^+-\text{CH}_3) > D^0(\text{Co}^+-\text{H})$  is unexpected since most metal-hydrogen bonds are stronger than metal-carbon  $\sigma$  bonds. The 9 kcal/mol difference here is attributed to the fact that a methyl group is substantially more polarizable than a hydrogen atom.<sup>28</sup>

We have implicitly assumed above that the structure of the species having the formula  $(\text{CoCH}_3)^+$  corresponds to a cobalt methyl ion. It is possible, however, that one (or more) of the hydrogens is actually bonded to the metal. Using the heats of formation,  $\Delta H_f^+(\text{CoCH}_3^+) = 256 \pm 4$  kcal/mol<sup>29</sup> and  $\Delta H_f^0(\text{CoCH}_3^+) = 289 \pm 7$  kcal/mol,<sup>14</sup> we can calculate that process 10 must have a heat of reaction of  $85 \pm 11$  kcal/mol. Since



$D^0(\text{Co}^+-\text{H}) = 52$  kcal/mol, it seems unlikely that a bond energy of 85 kcal/mol represents a cobalt-hydrogen bond but rather a C-H bond weakened by resonance stabilization of the  $\text{CoCH}_2^+$  product.<sup>30</sup>

Minor products observed in the  $\text{Co}^+$ -ethane system are  $\text{CoCH}_2^+$  and  $\text{CoC}_2\text{H}_4^+$ . The cross sections are of insufficient magnitude (less than  $0.2 \text{ \AA}^2$ ) to allow accurate analysis of thresholds. Qualitatively, the energy dependence of the cross section for formation of  $\text{CoCH}_2^+$  is similar to that of  $\text{CoCH}_3^+$ , peaking at about 4 eV. The  $\text{CoC}_2\text{H}_4^+$  product exhibits the lowest apparent threshold of all the products, <1 eV, and peaks at lower energies, about 3 eV. Energetic requirements establish that these minor products are formed in reactions 11 and 12.



The various processes which occur when  $\text{Co}^+$  interacts with ethane can now be understood and are outlined in Scheme I. The first step, oxidative addition of a C-H or C-C bond to  $\text{Co}^+$ , seems energetically feasible, considering the values for  $D^0(\text{Co}^+-\text{CH}_3)$  and  $D^0(\text{Co}^+-\text{H})$ . The lowest energy decomposition process for **3** and **4** is a rearrangement followed by reductive elimination of  $\text{H}_2$  or  $\text{CH}_4$ . While **4** can only rearrange by migration of an  $\alpha$ -hydrogen, **3** can rearrange by  $\alpha$ -H transfer to eventually form the cobalt ethylidene ion, by  $\alpha$ -Me transfer to yield the cobalt carbene ion, or by  $\beta$ -H transfer to form a cobalt ion-ethene complex. Assuming  $D^0(\text{CH}_2\text{Co}^+-\text{H}) = D^0(\text{Co}^+-\text{H})$ , we calculate the energy necessary to transfer an  $\alpha$ -hydrogen from the carbon

(28) Differences between the methyl and hydrogen bond energies,  $D^0(\text{X}^+-\text{CH}_3) - D^0(\text{X}^+-\text{H})$ , for the halide ions, X = I, Br, and Cl, are 5, 7 and 13 kcal/mol, respectively.

(29) This heat of formation may be calculated without prior assumption about the structure of the ion directly from the endothermicity of reaction 9.

(30)  $D^0(\text{H}-\text{C}_2\text{H}_5) = 86.6$  kcal/mol.  $D^0(\text{H}-\text{CH}_2\text{C}_2\text{H}_5) = 87.9$  kcal/mol. D. M. Golden, *J. Am. Chem. Soc.*, **101**, 1230 (1979).

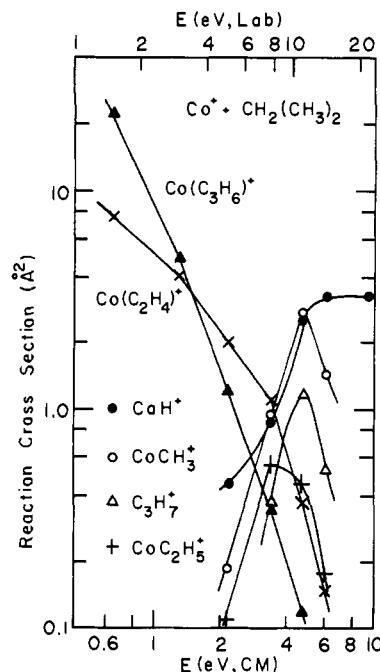
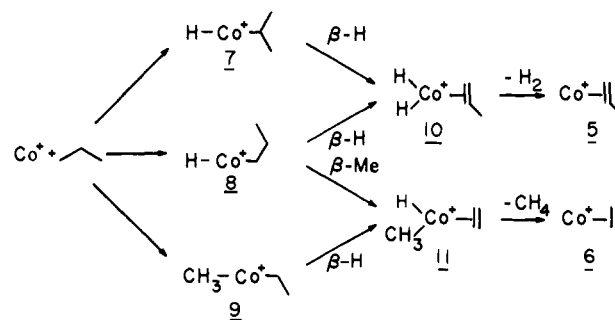


Figure 4. Variation in experimental cross section for the interaction of  $\text{Co}^+$  with propane as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale).

Scheme II



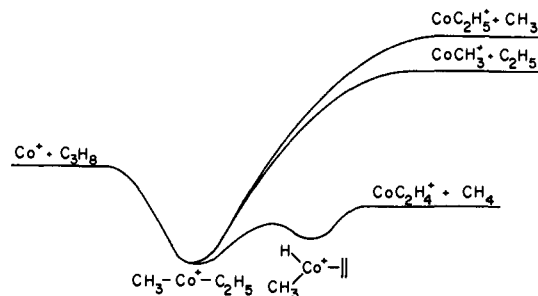
of  $\text{CoCH}_3^+$  to the metal as 33 kcal/mol, which is above the approximate threshold for production of  $\text{CoC}_2\text{H}_4^+$ . The  $\alpha$ -alkyl shift is considered an equally unfavorable process. Evidence presented below indicates that the  $\beta$ -H transfer, however, is quite facile.<sup>4,5</sup> Thus, in analogy with related studies in solution,<sup>31</sup> we conclude that  $\beta$ -H migration dominates rearrangement of intermediates such as **3**. This implies that the structure of  $\text{CoC}_2\text{H}_4^+$  is a cobalt ion-ethene complex. At higher energies, **3** and **4** decompose by more direct routes involving fission of a metal-carbon bond. Such processes have higher frequency factors than rearrangement<sup>32</sup> and thus are the only important reactions once energetically allowed.

**Reaction of  $\text{Co}^+$  with Deuterated Ethanes.** The magnitude and behavior as a function of energy of the cross section for reaction of cobalt ions with  $\text{C}_2\text{D}_6$  or  $\text{CH}_3\text{CD}_3$  are the same as with  $\text{C}_2\text{H}_6$ , within experimental error. In the reaction with  $\text{CH}_3\text{CD}_3$ , the only cobalt methyl ion species formed are  $\text{CoCH}_3^+$  and  $\text{CoCD}_3^+$ . These two products have similar cross sections (within  $\pm 20\%$ ) at all energies. This is also true for the cobalt carbene ion products,  $\text{CoCH}_2^+$  and  $\text{CoCD}_2^+$ , and the cobalt hydride ion products,  $\text{CoH}^+$  and  $\text{CoD}^+$ . The isotopic composition of the cobalt ion-ethene complex could not be determined due to a low signal intensity.

**Reaction of  $\text{Co}^+$  with Propane.** Results for the interaction of cobalt ions with propane are shown in Figure 4. Unlike the data

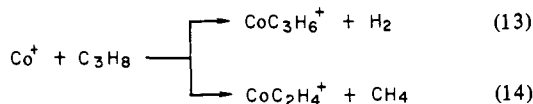
(31) R. R. Schrock and G. W. Parshall, *Chem. Rev.*, **76**, 243 (1976).

(32) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley, London, 1972.



**Figure 5.** Postulated reaction coordinate energy diagram for oxidative addition of the carbon-carbon bond of propane to cobalt ions.

discussed above, the reaction cross sections are large and decrease monotonically with increasing energy. This indicates that reactions 13 and 14, which yield **5** and **6** (Scheme II), are exothermic.



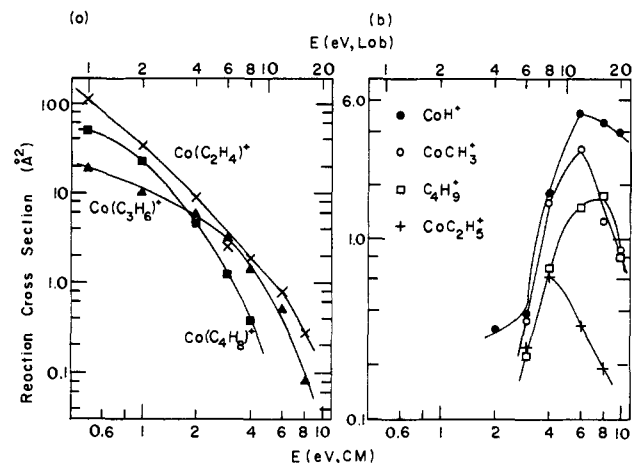
Energetic requirements stipulate the neutral products indicated. This typifies the behavior observed for reaction of  $\text{Co}^+$  with all larger alkanes. Also typical is the high-energy region shown in Figure 4, where endothermic channels yield a variety of products.

We can understand the reactions of  $\text{Co}^+$  with propane by again postulating initial oxidative addition of a C-H or C-C bond to cobalt ions (Scheme II). The intermediates formed, **7**, **8**, and **9**, undergo further reaction to yield **10** and **11** which reductively eliminate  $\text{H}_2$  and  $\text{CH}_4$ , respectively, giving the observed products. That **7**, **8**, or **9** rearrange by  $\alpha$ -H or  $\alpha$ -alkyl transfer is not considered likely, for reasons already discussed. Intermediate **8** could also rearrange by a  $\gamma$ -H transfer to the metal forming a metal-cyclobutane. This process, discussed in greater detail below, is also considered improbable.

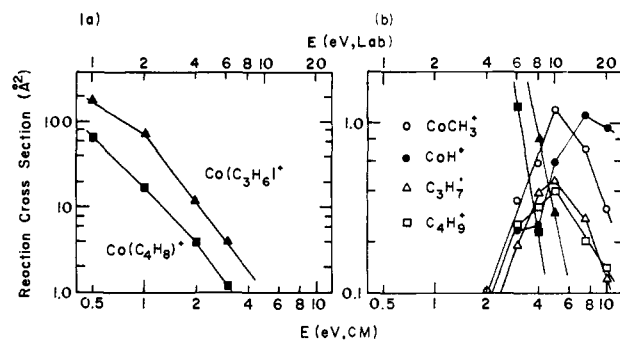
While Scheme II is definitely consistent with the products observed at low energies, it must also be capable of explaining products observed at higher energies. As discussed above, once endothermic bond fission processes become energetically accessible, they become the dominant decomposition routes of intermediates such as **7**, **8**, and **9**. A qualitative potential energy surface for intermediate **9** (Figure 5) exemplifies these considerations. Below about 1 eV, only the exothermic reaction involving rearrangement can occur. At higher energies, **9** can dissociate by cleavage of one of the cobalt-carbon bonds, the weakest in the complex. Formation of  $\text{CoCH}_3^+$  and  $\text{CoC}_2\text{H}_5^+$  at higher energies is taken as further evidence that oxidative addition of carbon-carbon bonds to  $\text{Co}^+$  occurs. Formation of these products would not be expected if formation of  $\text{CoC}_2\text{H}_4^+$  proceeded exclusively through intermediate **8** (Scheme II). While  $\beta$ -alkyl abstraction cannot be ruled out experimentally, this process is not required to explain the observed products.

**Reaction of  $\text{Co}^+$  with *n*-Butane and 2-Methylpropane.** The butanes represent the smallest isomeric alkanes. In addition, *n*-butane is the first alkane to have two types of carbon-carbon bonds. Results for the interaction of  $\text{Co}^+$  with *n*-butane and 2-methylpropane are shown in Figures 6 and 7, respectively. While the total cross sections are comparable, the product distributions are substantially different. Two products,  $\text{CoC}_2\text{H}_4^+$  and  $\text{CoC}_3\text{H}_6^+$ , corresponding to C-C bond cleavage are observed in the *n*-butane system, while only the latter product is seen in the 2-methylpropane case.

The high-energy products of the *n*-butane and 2-methylpropane systems are also distinct. Cobalt hydride ions and cobalt methyl ions dominate both systems, but cobalt ethyl ions are observed only in reaction with *n*-butane. In this system,  $\text{C}_4\text{H}_9^+$  is the major alkyl ion observed while  $\text{C}_3\text{H}_7^+$  and  $\text{C}_2\text{H}_5^+$  are minor products (not shown in Figure 6). In reaction with 2-methylpropane,  $\text{C}_4\text{H}_9^+$  and  $\text{C}_3\text{H}_7^+$  are formed in comparable yields and  $\text{C}_2\text{H}_5^+$  is not seen. A mechanism analogous to Scheme II explains both the low- and high-energy results.

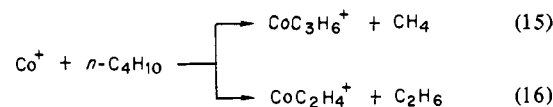


**Figure 6.** Variation in experimental cross section for the interaction of  $\text{Co}^+$  with *n*-butane as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). Part a shows exothermic channels; part b shows endothermic channels. Note change of scale.



**Figure 7.** Variation in experimental cross section for the interaction of  $\text{Co}^+$  with 2-methylpropane as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). Part a shows exothermic channels; part b shows endothermic channels. Note change of scale.

The relative yield for reaction 15 is one-fifth that of reaction 16. Yet, since the binding energy of propene to  $\text{Co}^+$  should be

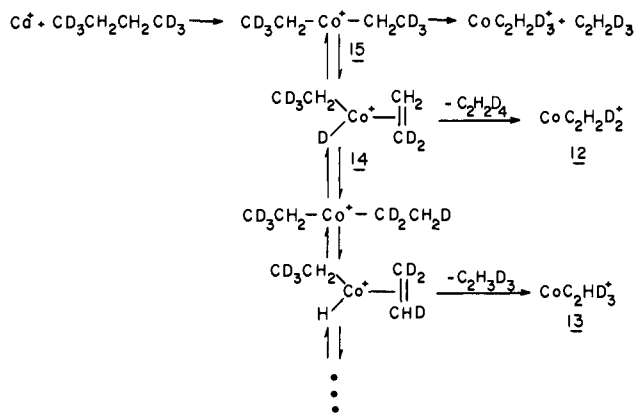


greater than that of ethene,<sup>33</sup> process 15 should be more exothermic than 16. This result suggests that the product distribution is determined by the initial oxidative addition since the internal C-C bond in *n*-butane is weaker than the terminal bond by about 6 kcal/mol.<sup>26</sup>

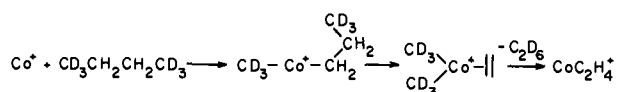
**Reaction of  $\text{Co}^+$  with Deuterated Butanes.** The reaction of  $\text{Co}^+$  with butane-*1,1,1,4,4,4-d*<sub>6</sub>,  $\text{CD}_3\text{CH}_2\text{CH}_2\text{CD}_3$ , was examined to further elucidate the mechanism of the alkane reactions. The cobalt ion ethene complex product exemplifies the results. Only the  $\text{Co}(\text{C}_2\text{H}_2\text{D}_2)^+$  (**12**) and  $\text{Co}(\text{C}_2\text{HD}_3)^+$  (**13**) species are detected in a 3:1 ratio at the lowest energies. As the collision energy is raised, the latter product decreases until only the former is observed. At the highest energies, the only cobalt ethyl ion seen is  $\text{CoC}_2\text{H}_2\text{D}_3^+$ . Scheme III proposes a mechanism to explain these results. A statistical distribution of products **12** and **13** is predicted by this mechanism to be 3:2. This is an obvious limit on the actual behavior since hydrogen scrambling must proceed via intermediate

(33) This conclusion is based on the exothermicity of reaction 13 which suggests  $D^\circ(\text{Co}^+-\text{C}_3\text{H}_6) > 30$  kcal/mol, the endothermicity of reaction 12 which suggests  $D^\circ(\text{Co}^+-\text{C}_2\text{H}_4) < 33$  kcal/mol, and the exothermicity of reactions with larger alkanes (2-methyl-butane and 2,2-dimethylbutane) which yield  $\text{CoC}_3\text{H}_6^+$  suggesting that  $D^\circ(\text{Co}^+-\text{C}_2\text{H}_4) > 24$  kcal/mol. Thermochemical data are from ref 26.

## Scheme III



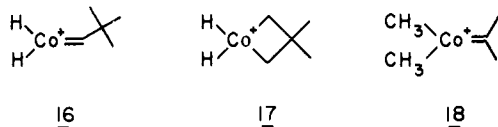
## Scheme IV



14. As the interaction energy increases, decomposition of 14 to 12 precludes further rearrangement. Eventually, decomposition of 15 to  $\text{CoC}_2\text{H}_2\text{D}_3^+$  dominates the reaction. We conclude that  $\beta$ -H transfer to and from the metal is facile. It is noted that scrambling of all ten hydrogens in the butane does not occur; no  $\text{CoC}_2\text{H}_4^+$ ,  $\text{CoC}_2\text{H}_3\text{D}^+$ , or  $\text{CoC}_2\text{D}_4^+$  products are detected. This observation also provides evidence that  $\beta$ -alkyl transfer is unlikely, since if this were a viable process, formation of  $\text{CoC}_2\text{H}_4^+$  should occur (Scheme IV).

The cobalt propene ion and cobalt butene ion products also exhibit hydrogen scrambling. However, low signal intensity precluded obtaining data as accurate as that for the cobalt ethene ion product. The predominant propene complex product is  $\text{Co}(\text{C}_3\text{H}_3\text{D}_3)^+$  (>75% at 0.5 eV and ~100% above 1 eV), consistent with a mechanism like Scheme III. At higher energies, the only cobalt methyl ion observed is the perdeuterated species. The dehydrogenation reaction to form cobalt butene ion consists of loss of  $\text{H}_2$ , HD, and  $\text{D}_2$  with no discernible energy effect. Both  $\text{CoH}^+$  and  $\text{CoD}^+$  are observed at higher energies.

**Reaction of  $\text{Co}^+$  with 2,2-Dimethylpropane.** The results for the reaction of  $\text{Co}^+$  with 2,2-dimethylpropane are shown in Figure 8. Observation of a single low-energy product,  $\text{CoC}_4\text{H}_8^+$ , is entirely consistent with oxidative addition of a C-C bond to  $\text{Co}^+$ ,  $\beta$ -H abstraction, and reductive elimination of  $\text{CH}_4$ . Formation of 16, 17, and 18, which require  $\alpha$ -H transfer,  $\gamma$ -H transfer, and



$\alpha$ -Me transfer, respectively, do not appear to occur as no  $\text{CoC}_5\text{H}_{10}^+$ , formed by reductive elimination of  $\text{H}_2$  from 16 or 17, or  $\text{CoC}_3\text{H}_5^+$ , formed by reductive elimination of  $\text{C}_2\text{H}_6$  from 18, is observed. This presumes, as seems likely, that reductive elimination is competitive with other decomposition reactions of 16, 17, and 18, including reverting to reactants.

**Bond Energies of  $\text{CoH}$  and  $\text{CoCH}_3$ .** As discussed above, the intermediates formed by the initial oxidative addition decompose at high energies by simple bond fission forming both cobalt alkyl ions or cobalt hydride ions and alkyl ions. In the dissociation of such a charged intermediate, the preferred ionic product is the fragment having the lower ionization potential (IP).<sup>34,35</sup> Thus,  $\text{C}_3\text{H}_7^+$  is formed in lower abundance in the *n*-butane system than in the 2-methylpropane system because  $\text{IP}(n\text{-C}_3\text{H}_7) = 8.16 \text{ eV}$ <sup>36</sup>

(34) Sometimes referred to as Stevenson's Rule,<sup>35</sup> this observation is a straightforward conclusion of RRKM theory.<sup>32</sup>

(35) D. P. Stevenson, *Discuss. Faraday Soc.*, **10**, 35 (1951).

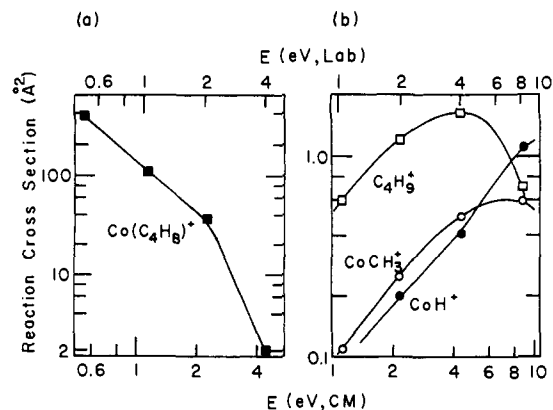
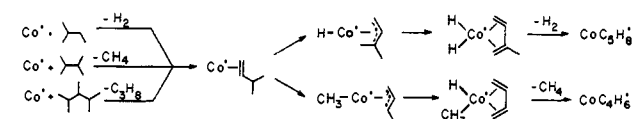


Figure 8. Variation in experimental cross section for the interaction of  $\text{Co}^+$  with 2,2-dimethylpropane as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). Part a shows exothermic channels; part b shows endothermic channels. Note change of scale.

## Scheme V



>  $\text{IP}(i\text{-C}_3\text{H}_7) = 7.36 \text{ eV}$ .<sup>37</sup> In addition, in both systems, the complementary product  $\text{CoCH}_3^+$  is formed in greater yield than  $\text{C}_3\text{H}_7^+$ , implying  $\text{IP}(\text{CoCH}_3) < 7.36 \text{ eV}$ . Similarly, in reaction with 2,2-dimethylpropane,  $\text{C}_4\text{H}_9^+$  is the dominant product, suggesting  $\text{IP}(\text{CoCH}_3) > \text{IP}(t\text{-C}_4\text{H}_9) = 6.70 \text{ eV}$ .<sup>37</sup> When such considerations are applied to all systems investigated, the ionization potentials obtained are  $7.0 \pm 0.3 \text{ eV}$  for  $\text{CoCH}_3^+$ <sup>38</sup> and  $7.3 \pm 0.1 \text{ eV}$  for  $\text{CoH}^+$ .<sup>44</sup> (Table I).<sup>45</sup>

Using these ionization potentials and the bond energies for  $\text{CoH}^+$  and  $\text{CoCH}_3^+$  given in Table I, we may calculate the bond energies of the neutral  $\text{CoH}$  and  $\text{CoCH}_3$  species to be  $39 \pm 6 \text{ kcal/mol}$  and  $41 \pm 10 \text{ kcal/mol}$ , respectively. The fact that these values are comparable lends credence to the idea that polarizability effects are responsible for the larger cobalt methyl bond energy in the ion. The value for  $D^\circ(\text{CoCH}_3)$  is comparable to other known metal-methyl bond energies such as  $D^\circ(\text{CH}_3\text{-Mn}(\text{CO})_5) \approx 29 \text{ kcal/mol}$ ,<sup>46</sup>  $D^\circ(\text{CH}_3\text{-Re}(\text{CO})_5) = 53.2 \pm 2.5 \text{ kcal/mol}$ ,<sup>46</sup> and  $D^\circ[(\text{CH}_3)_2(\pi\text{-C}_3\text{H}_5)\text{Pt-CH}_3] = 39 \pm 5 \text{ kcal/mol}$ .<sup>47</sup>

The value for  $D^\circ(\text{CoH})$  is in the same range as the bond energy for the isoelectronic species  $\text{NiH}^+$  ( $43 \pm 2 \text{ kcal/mol}$ ),<sup>19</sup> that of  $\text{FeH}$  ( $39 \pm 7 \text{ kcal/mol}$ ),<sup>48</sup> and theoretical estimates for  $\text{ScH}$  ( $42$

(36) F. A. Houle, Ph.D. Thesis, California Institute of Technology, 1979.

(37) F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, **101**, 4067 (1979).

(38)  $\text{IP}(s\text{-C}_4\text{H}_9) \approx 7.25 \text{ eV} > \text{IP}(\text{CoCH}_3) > \text{IP}(t\text{-C}_4\text{H}_9) = 6.70 \text{ eV}$ .<sup>37</sup>

(39) This value is lowered from Lossing's value of  $7.41 \text{ eV}$ <sup>40</sup> by the discrepancy between Lossing's value for  $\text{IP}(i\text{-C}_3\text{H}_7) = 7.55 \text{ eV}$ <sup>40</sup> and that of Houle and Beauchamp,  $7.36 \text{ eV}$ .<sup>37</sup> Lossing's values correspond more nearly to the vertical rather than the adiabatic ionization potential.

(40) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

(41)  $\text{IP}(i\text{-C}_3\text{H}_7) = 7.36 \text{ eV} > \text{IP}(\text{CoH}) > \text{IP}(n\text{-C}_3\text{H}_7) = 7.21 \text{ eV}$ .<sup>43</sup>

(42) P. B. Armentrout and J. L. Beauchamp, to be submitted for publication.

(43) F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, submitted for publication.

(44) Comparison of  $\text{CoH}^+$  to the complementary alkyls must be made at the lowest possible energies to minimize the amount of  $\text{CoH}^+$  formed by direct hydrogen abstraction.

(45) More conservatively, these ionization potentials may be considered lower limits. This is because "direct" reactions having higher frequency factors may result in anomalously high yields of  $\text{CoH}^+$  and perhaps  $\text{CoCH}_3^+$  compared to that expected on a purely energetic basis. This possibility also suggests that the values derived for  $D^\circ(\text{CoH})$  and  $D^\circ(\text{CoCH}_3)$  may be too low.

(46) D. L. S. Brown, J. A. Connor, and H. A. Skinner, *J. Organomet. Chem.*, **81**, 403 (1974).

(47) K. W. Egger, *J. Organomet. Chem.*, **24**, 501 (1970).

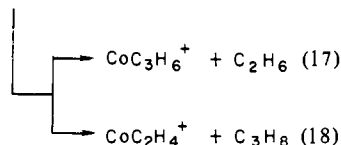
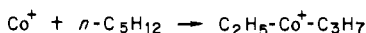
(48) A. Dendramis, R. J. Van Zee, and W. Weltner, Jr., *Astrophys. J.*, **231**, 632 (1979).

kcal/mol)<sup>49</sup> and TiH (37 kcal/mol).<sup>49</sup> Interestingly, it is substantially weaker than  $D^{\circ}[\text{H}-\text{Co}(\text{CO})_4] = 54 \pm 9$  kcal/mol, implying the carbonyls exert a strong substituent effect.

The comparison of bond energies in high spin coordinatively unsaturated species<sup>51</sup> (e.g., CoH) with closed-shell diamagnetic species [e.g.,  $\text{HCo}(\text{CO})_4$ ] is likely to be hazardous at best. Electron donation from the filled  $e_2$  bonding orbital of the methyl group into partially filled or vacant orbitals on the metal with  $\pi$  symmetry may result in an increase in  $D^{\circ}(\text{Co}-\text{CH}_3)$  relative to  $D^{\circ}(\text{Co}-\text{H})$ . The small difference in these bond energies is in marked contrast to the difference  $D^{\circ}[\text{H}-\text{Mn}(\text{CO})_5] - D^{\circ}[\text{CH}_3-\text{Mn}(\text{CO})_5] \approx 30$  kcal/mol.<sup>52</sup> Reaction calorimetric measurements in solution give  $D^{\circ}[\text{M}-\text{H}] - D^{\circ}[\text{M}-\text{CH}_3] \approx 25$  kcal/mol for  $\text{M} = \text{Mo}$  and  $\text{W}$  in the complexes  $(\eta^3\text{-C}_3\text{H}_5)\text{MX}_2$  where  $\text{X} = \text{H}$  or  $\text{CH}_3$ .<sup>53</sup> Bond enthalpy contributions  $\bar{D}(\text{Mo}-\text{H}) = 60$  and  $\bar{D}(\text{W}-\text{H}) = 73$  kcal/mol are estimated for these complexes.

**Reaction of  $\text{Co}^+$  with Larger Alkanes,  $\text{C}_n\text{H}_{2n+2}$  ( $n = 5-8$ ).** The product distributions of the reactions of cobalt ions with several large alkanes at low energy are given in Table II. With few exceptions, these results may be explained by initial oxidative addition of a C-C or C-H bond, followed by  $\beta$ -H abstraction and reductive elimination of a neutral yielding a cobalt alkene ion. If sufficient internal energy is retained by this complex, further reaction may occur to yield a cobalt ion-alkadiene complex. The mechanism for this process begins by insertion of the  $\text{Co}^+$  into an allylic C-C or C-H bond followed again by  $\beta$ -H abstraction and reductive elimination.<sup>54</sup> An example, the further reaction of  $\text{Co}(3\text{-methyl-1-butene})^+$ , is illustrated in Scheme V.

Qualitative trends in the product distributions are well accounted for by the proposed mechanism and simple thermochemical arguments. As discussed above, the initial oxidative addition occurs preferentially with the weakest bonds of the alkane. Thus, production of methane, resulting from insertion of  $\text{Co}^+$  into terminal C-C bonds, occurs less frequently than the reactions from insertion into internal C-C bonds. Highly substituted alkenes are bound to  $\text{Co}^+$  more tightly than smaller alkenes.<sup>33</sup> Thus, cleavage of the internal bond of 2-methylbutane or 2,2-dimethylbutane results preferentially in formation of  $\text{CoC}_2\text{H}_6^+$  and  $\text{CoC}_4\text{H}_8^+$ , respectively, rather than  $\text{CoC}_2\text{H}_4^+$ , even when normalized for the different number of  $\beta$ -hydrogens. Transfer of secondary and tertiary  $\beta$ -hydrogens is found to be more likely than primary  $\beta$ -H transfer. Thus, for  $n$ -pentane (and all larger  $n$ -alkanes), products due to reaction 17 (secondary  $\beta$ -H transfer) are more prevalent than those from reaction 18 (primary  $\beta$ -H transfer), even when accounting



for the different numbers of the two types of  $\beta$ -hydrogens and the binding energy effect discussed above. An analysis of the

(49) K. P. Huber and G. Herzberg, "Constants of Diatomic Molecules", Van Nostrand, New York, 1979.

(50) This value is calculated from  $\Delta H_f^{\circ}[\text{Co}_2(\text{CO})_8(\text{g})] = -281 \pm 3$  kcal/mol [P. J. Gardner, A. Cartner, R. G. Cunninghame, and B. H. Robinson, *J. Chem. Soc., Dalton Trans.*, 2583 (1975); J. A. Connor, H. A. Skinner, and Y. Virmani, *Faraday Symp. Chem. Soc.*, 8, 18 (1972)],  $\Delta H_f^{\circ}[\text{HCo}(\text{CO})_4(\text{g})] = -136 \pm 5$  kcal/mol [Yu. E. Bronshtein, V. Y. Gankin, D. P. Prinkin, and D. M. Rudovskii, *Russ. J. Phys. Chem. (Engl. Transl.)* 40, 802 (1966)], and  $D^{\circ}[(\text{CO})_4\text{Co}-\text{Co}(\text{CO})_4] = 12 \pm 5$  kcal/mol [D. R. Bidinosti and N. S. McIntyre, *Chem. Commun.*, 1 (1967); *Can. J. Chem.*, 48, 593 (1970)].

(51) R. J. Van Zee, C. M. Brown, K. J. Zeringue, and W. Weltner, Jr., *Acc. Chem. Res.*, 13, 237 (1980).

(52) Recent ICR studies support a smaller difference for these bond energies, possibly as low as 5 kcal/mol. These results are being refined (A. E. Stevens and J. L. Beauchamp, unpublished results).

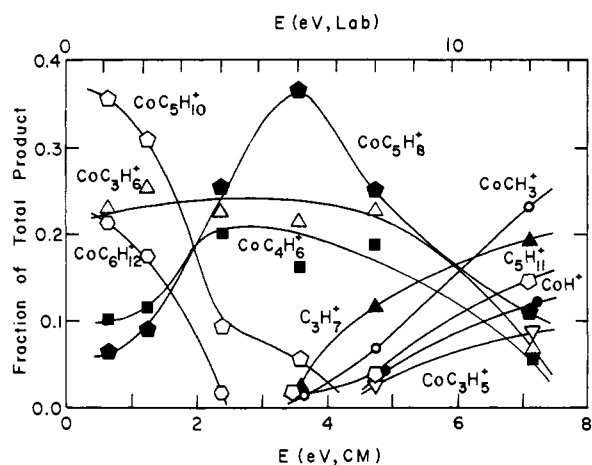
(53) J. C. G. Calado, A. R. Dias, J. A. M. Simoes, and M. A. V. R. DaSilva, *J. Organomet. Chem.*, 174, 77 (1979).

(54) This process has been observed previously. See, for example, ref 4 and 5.

Table II. Product Distributions of Exothermic Reactions of  $\text{Co}^+$  with Alkanes Measured at  $\sim 1\text{-eV}$  Relative Kinetic Energy<sup>a</sup>

reactant alkane	structure	neutral products ( $\text{C}_m\text{H}_{2m+2}$ ) corresponding to ionic products, $\text{Co}(\text{C}_{n-m}\text{H}_{2(n-m)})^+$										neutral products corresponding to $\text{Co}(\text{alkadiene})^+$ products				
		$\text{H}_2$	$\text{CH}_4$	$\text{C}_2\text{H}_6$	$\text{C}_3\text{H}_8$	$\text{C}_4\text{H}_{10}$	$\text{C}_5\text{H}_{12}$	$\text{C}_6\text{H}_{14}$	$2\text{H}_2$	$\text{H}_2 + \text{CH}_4$	$\text{H}_2 + \text{C}_2\text{H}_6$	$\text{H}_2 + \text{C}_3\text{H}_8$	$\text{H}_2 + \text{C}_4\text{H}_{10}$	$\text{CH}_4 + \text{C}_3\text{H}_8$	$2\text{C}_2\text{H}_6$	
$\text{C}_3\text{H}_8$	propane	0.59	0.41													
$\text{C}_4\text{H}_{10}$	butane	0.29	0.12	0.59												
	2-methylpropane	0.23	0.77													
$\text{C}_5\text{H}_{12}$	pentane	0.30	0.02	0.59	0.08											
	2-methylbutane	0.20	0.37	0.27	0.05											
	2,2-dimethylpropane		1.0													
$\text{C}_6\text{H}_{14}$	hexane	0.39	0.02	0.35	0.16	0.04										
	3-methylpentane	0.13	0.14	0.54	0.03*	0.05										
	2,2-dimethylbutane	0.12	0.30	0.40	0.03*	0.02										
	2,3-dimethylbutane	0.22	0.35	0.23	0.23											
$\text{C}_7\text{H}_{16}$	heptane	0.28	0.01	0.15	0.22	0.28	0.04									
	2,4-dimethylpentane	0.26	0.19	0.36	0.36	0.15										
	octane	0.24	<0.01	0.10	0.18	0.20	0.16	0.02								
$\text{C}_8\text{H}_{18}$	2,3,4-trimethylpentane	0.16	0.14	0.14*	0.29	0.14*	0.07									
	2,2,4-trimethylpentane	0.19	0.09	0.28	0.29	0.28	0.30									
	2,2,3,3-tetramethylbutane	0.07*	0.16	0.05*	0.05*	0.13										

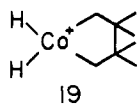
<sup>a</sup> Starred products are not accounted for by the general mechanism proposed in the text.



**Figure 9.** Variation in product distribution for the interaction of Co<sup>+</sup> with 2,3-dimethylbutane as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). Several minor products are omitted for clarity.

2,4-dimethylpentane system indicates a similar preference for tertiary vs. primary  $\beta$ -H transfer.

Products, starred in Table II, which cannot be explained by the proposed mechanism are generally minor and involve highly branched alkanes. Alkyl migration can explain some of these results. Skeletal rearrangement of the hydrocarbons may also be occurring. Another intriguing possibility suggested by the dehydrogenation of 2,2,3,3-tetramethylbutane is the formation of the metallocyclopentane **19**.



As the collision energy is raised, product distributions of Co<sup>+</sup> reacting with larger alkanes vary as would be expected. The example of 2,3-dimethylbutane, shown in Figure 9, is typical. Cross sections for the ionic products, CoC<sub>6</sub>H<sub>12</sub><sup>+</sup> and CoC<sub>5</sub>H<sub>10</sub><sup>+</sup>, are observed to decrease rapidly with increasing energies. This is presumably because the neutral products, H<sub>2</sub> and CH<sub>4</sub>, respectively, have few internal degrees of freedom and thus leave the cobalt alkene ion with more internal energy than ionic products formed in conjunction with larger neutral products. The cobalt alkadiene ion products, CoC<sub>5</sub>H<sub>8</sub><sup>+</sup> and CoC<sub>4</sub>H<sub>6</sub><sup>+</sup>, which are the result of secondary reactions, dominate the products at intermediate energies. At the highest energies, endothermic bond fission processes yield the observed results. As with the butanes, product distributions at these energies are sensitive to the structure of the reactant alkane.

A final elaboration of the general mechanism explains the observation of the CoC<sub>3</sub>H<sub>5</sub><sup>+</sup> product ion (Figure 9). In no system was any cobalt alkyl ion containing three or more carbons observed. We postulate that secondary dehydrogenation of such cobalt alkyl ions to yield cobalt allyl ions is a facile decomposition reaction.

## Conclusion

The reactions of Co<sup>+</sup> with hydrogen and alkanes comprise a cohesive set of experiments. The strengths of cobalt-hydrogen and cobalt-carbon bonds are determined to be sufficient that oxidative addition of a carbon-hydrogen or carbon-carbon bond

to Co<sup>+</sup> is energetically feasible. Thus, dehydrogenation and carbon-carbon bond cleavage reactions are observed to occur at thermal energies with large cross sections. However, Co<sup>+</sup> is not so reactive as to preclude selectivity. Product distributions are strongly dependent on alkane structure and interaction energy. Trends in reactivity can be rationalized by using thermodynamic arguments.

We have made a strong case for oxidative addition of carbon-carbon bonds to transition-metal ions as an initial step in a process which eventually results in rupture of the bond. The important evidence for our assertion is that a single mechanism consistently explains *both* low- and high-energy products for all alkanes examined. Thus, the high-energy products result from dissociation of the same reaction intermediates invoked to explain products observed at low energies. This conclusion is admittedly equivocal, and unfortunately deuterium or <sup>13</sup>C labeling cannot distinguish this mechanism for carbon-carbon bond cleavage from that involving initial insertion into carbon-hydrogen bonds followed by  $\beta$ -alkyl shifts. However, the high-energy products are not easily explained by this second possibility.

The studies described above indicate that a significant amount of chemistry may occur on a *single* metal center. The reactions may be viewed as catalytic processes resulting in the cracking and dehydrogenation of alkanes. The activation energy of these reactions is equivalent to the binding energy of an alkene to Co<sup>+</sup>. Thus, conversion of alkanes to alkenes and smaller alkanes requires about 25–40 kcal/mol which is utilized in regenerating the "catalyst". This energy is comparable to activation energies observed for hydrogenolysis of alkanes on platinum surfaces.<sup>55</sup> Interestingly, surface studies have invariably considered that reaction involves simultaneous interaction with several atoms.<sup>56</sup> Evidently this is not a requirement, and a single site with several coordination vacancies may suffice.<sup>57</sup>

The present work has focused on the reactions of Co<sup>+</sup> (d<sup>8</sup>, <sup>3</sup>F ground state). Related studies suggest that the reactivity of Fe<sup>+</sup> (d<sup>7</sup>, <sup>4</sup>F ground state) and Ni<sup>+</sup> (d<sup>9</sup>, <sup>2</sup>D ground state) are similar.<sup>5,58</sup> In comparison to these group 8 transition-metal ions, the species Cr<sup>+</sup> (d<sup>5</sup>, <sup>6</sup>S ground state) and Mn<sup>+</sup> (s<sup>1</sup>d<sup>5</sup>, <sup>7</sup>S ground state) are unreactive.<sup>57</sup> The atomic ion Rh<sup>+</sup> (d<sup>8</sup>, <sup>3</sup>F ground state) reacts at low energies exclusively to dehydrogenate hydrocarbons, including ethane. Reactions involving carbon-carbon bond cleavage are not observed.<sup>58</sup> This is also the case for the 14-electron cyclopentadienyl complex ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ni<sup>+</sup>, which readily dehydrogenates hydrocarbons but does not effect bond cleavage processes characteristic of the atomic reactant Ni<sup>+</sup>.<sup>4</sup>

Assessing the importance of factors such as charge, electronic configuration, and spin state, as well as the degree and type of substitution on the thermochemical properties and reactivity of particular transition metals, will require additional study. Current endeavors in our laboratory are addressing these problems.

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