Cobalt carbene ion: Reactions of Co+ with C2H4, cyclo-C3H6, and cyclo-C2H4O

P. B. Armentrout and J. L. Beauchamp

*Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125*
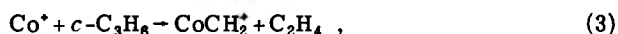
An ion beam apparatus is employed to study the formation of the cobalt carbene ion, $CoCH_2^+$. This ion is produced in the endothermic reaction of cobalt ions with ethene and cyclopropane and in an exothermic reaction with ethylene oxide. A model is proposed to account for the dependence of experimental cross sections on relative kinetic energy for the endothermic reactions. Using this model to interpret the experimental results, a bond dissociation energy $D°(Co^+-CH_2) = 3.7 \pm 0.3$ eV is derived.

I. INTRODUCTION

Transition metal carbenes have been postulated as intermediates in a variety of reactions, including metal alkyl decomposition,[1] olefin metathesis,[2] polymerization of olefins,[3] olefin homologation,[4] and cyclopropane formation from olefins.[5] Yet, despite their seeming abundance, little is known about metal carbene thermochemistry. Recently, ion cyclotron resonance spectroscopy was used in our laboratories to prepare several ionic carbenes of iron[6] and manganese[7] in the gas phase. These studies included the first experimental determinations of metal carbene bond dissociation energies. The present investigation represents a continuation of our effort to characterize metal carbenes in the gas phase. Specifically, we have studied the endothermic reactions of Co+ with ethene,

$$Co^+ + C_2H_4 \begin{cases} \rightarrow CoH^+ + C_2H_3 & (1) \\ \rightarrow CoCH_2^+ + CH_2 & (2) \end{cases}$$
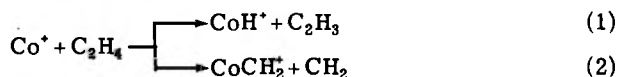
and with cyclopropane,

$$Co^+ + c\text{-}C_3H_6 \rightarrow CoCH_2^+ + C_2H_4 , \qquad (3)$$

and the exothermic reaction with ethylene oxide,

$$Co^+ + c\text{-}C_2H_4O \rightarrow CoCH_2^+ + CH_2O . \qquad (4)$$

The experimentally determined threshold for Reaction (2) is used in the present work to arrive at the cobalt carbene bond dissociation energy.

A complete understanding of the dynamics of such reactions requires knowledge of the potential energy surface. Due to the unavailability of such detailed information, a simple surface consisting of only the reaction coordinate is often considered. The dynamics of chemical reactions are often dominated by the gross features of such a simplified surface.[8] Speculation on the reaction coordinate diagrams for processes (2)–(4) reveals important features which distinguish these reactions. In Fig. 1(a), the example of a highly endothermic process, Reaction (2), is given. Even though the binding energy of Co+ to ethene is substantial, giving rise to a potential well,[9] a considerable amount of energy must be provided to surmount the reaction barrier. At these energies, the influence of the well on the reaction dynamics is small, and, therefore, we expect the reaction to be direct. The endothermicity of Reaction (3), Fig.

1(b), is much less. Based on related studies,[10] the formation of a metallocyclobutane as a reaction intermediate is proposed. The well corresponding to this reaction intermediate should be of comparable magnitude to the heat of reaction. This situation is more conducive to the formation of a long-lived complex which can dissociate in many ways including back to reactants. Finally, we consider a case where the reaction is exothermic, Fig. 1(c). A long-lived intermediate is again expected, but now formation of products is much more likely.

In the present study, a particular form for the excitation function of endothermic reactions is proposed. This form is used to analyze the dependence of the cross section for Reaction (2) on kinetic energy of the reactant
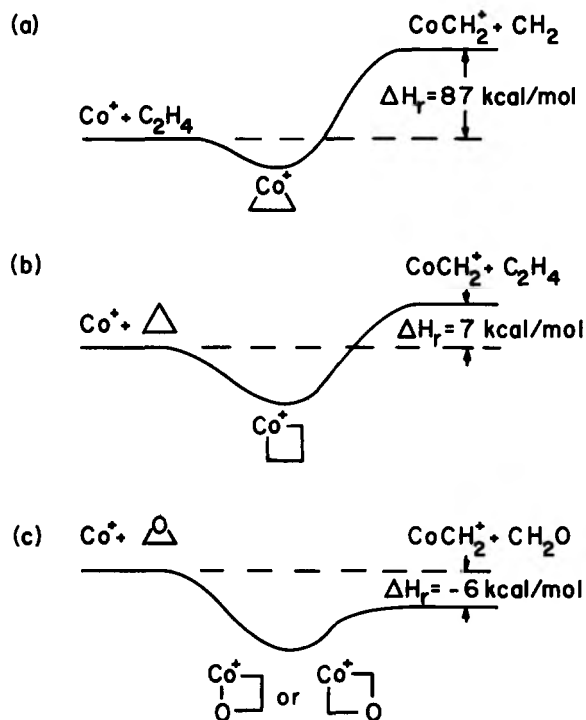

FIG. 1. Postulated reaction coordinate diagrams for Reaction (2), part (a), Reaction (3), part (b), and Reaction (4), part (c). The heats of reaction are determined in the present study. The scale of part (a) is a factor of 6 less than parts (b) and (c).
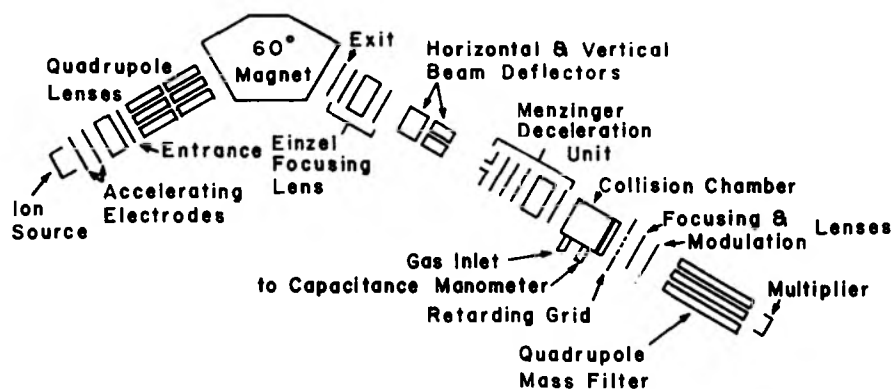
FIG. 2. Schematic diagram of the ion beam apparatus.

ion. Previously, the analyses of such processes concentrated on interpretation of the threshold region. In this paper, we have extended this analysis to include the energy region where substantial product dissociation may occur.[11] The proposed form for the reaction cross section is shown to fit the experimental results over a large energy range. The threshold measured for Reaction (2), using this analysis, allows us to derive the bond dissociation energy, $D^0(Co^+-CH_2) = 85 \pm 7$ kcal/mol. This agrees with the upper limit for this bond energy of 92 kcal/mol established by the endothermicity of Reaction (3) and with the lower limit of 79 kcal/mol established by the exothermicity of Reaction (4). The agreement gives us confidence that the analysis is useful in obtaining accurate thermochemical data.

II. EXPERIMENTAL

The ion beam apparatus shown in Fig. 2 is a highly modified version of an instrument previously described.[12] Ions from a surface ionization source are accelerated (typically to about 700 V) and focused into a 60° sector magnet for mass separation. The ion beam mass selector provides unit mass resolution to greater than 100 m/z. This mass selected beam is decelerated and focused into a collision chamber containing the reactant gas. Product ions scattered in the forward direction are focused into a quadrupole mass filter and detected 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 ion source, previously described,[12] is comprised of a tubular stainless steel oven attached to the side of a U-shaped repeller plate which surrounds a rhenium ionization filament. For these experiments, the oven is loaded with $CoCl_2 \cdot 6H_2O$. The filament generates sufficient heat to dehydrate the cobalt complex and vaporize the $CoCl_2$. This vapor is directed at the filament where dissociation and ionization of the resulting Co takes place. This method of ionization minimizes the production of excited metal ion states. It is estimated that at the filament temperature used, ~2500 °K, 81% of the Co^+ ions produced are in the ^3F ground state manifold and 19% are in the ^5F excited state manifold at 0.42 eV. In order to observe the effects of an excited state, its lifetime must exceed about 10 μs, the approximate flight time of the ions. An attempt was made to determine the

presence of excited ions using an attenuation technique.[13,14] Only a single component was detected, suggesting that excited ions are absent. This assumes that the ^3F and ^5F states have different total scattering cross sections for the collision gases used (O_2, C_2H_4, and C_2H_6).

The energy of the ion beam is taken nominally as the difference in potential between the collision chamber and the center of the filament, the latter being determined by a resistive divider. This energy is verified by use of a retarding field energy analyzer.[15] Agreement was always within 0.3 eV. The energy width of the Co^+ beam was also thus obtained and determined to be 0.7 eV [full width at half-maximum (FWHM)]. In the center of mass frame, this introduces an uncertainty of ±0.12 eV in the reaction with C_2H_4 and of ±0.15 eV with $c-C_3H_6$ and $c-C_2H_4O$. No specific account of the energy distribution of the ion beam is taken in the treatment below.

Despite attempts to make such measurements, we find the present apparatus is not particularly suited to accurate determinations of product ion energies.[15] Severe problems due to focusing effects preclude an effective analysis on any ion having low intensity and a wide spread in kinetic energy. These effects may be accounted for if the ion is sufficiently intense and nearly monoenergetic (as for the incident ion beam).

A more severe problem concerning the actual energy of interaction is the effect of the thermal motion of the reactant gas. Chantry[16] has shown that the distribution of the relative kinetic energy at an energy E due to this effect has a full width at half-maximum of

$$W_{1/2} = (11.1 \gamma k T E)^{1/2} , \tag{5}$$

where T is the temperature of the target gas, and $\gamma = m/(m+M)$, m and M being the masses of the incident particle and target gas. Thus, $W_{1/2} = 0.44E^{1/2}$ eV for the reactions with ethene and $W_{1/2} = 0.41E^{1/2}$ for reaction with cyclopropane or ethylene oxide. This energy distribution effectively broadens any sharp features in the excitation function, including threshold. To account for this effect, the proposed excitation function is convoluted with this distribution before comparison with the data using the method outlined by Chantry.[16]

Reaction cross sections for a specific product, σ_i, are calculated from

$$\sigma_i = \frac{\sigma I_i}{\sum I_i} , \qquad (6)$$

where the sum is over all products and I_i refers to a particular measured product ion intensity. The total reaction cross section, σ, is evaluated using

$$I_0 = \left(I_0 + \sum I_i\right) \exp(-n\sigma l) , \qquad (7)$$

where I_0 is the transmitted reactant ion beam intensity, n is the number density of the target gas, and l is the length of the interaction region. The pressure of the target gas, measured using an MKS Baratron Model 90H1 capacitance manometer, is kept sufficiently low, $(1-5)\times10^{-3}$ Torr, that attenuation of the ion beam is minimal. The length of the interaction region is 5 mm and is uncorrected for entrance and exit apparature effects[17] (1.0 and 1.5 mm in diameter, respectively). Our experimental procedure is to take a complete scan of kinetic energy at a single pressure to obtain the excitation function. At several energies, the product yield is measured as a function of pressure to ensure Eqs. (6) and (7) are obeyed. This procedure also readily identifies products formed by more than one collision event.[18]

The greatest uncertainty in measurements of reaction cross sections is the ion detection efficiency. In the present experiments which involve heavy projectile and light target species, efficient detection is assisted by the appreciable center-of-mass velocity which tends to scatter all products in the forward direction in the laboratory frame. At laboratory energies below about 10 eV, a small field of 0.5 V is placed across the specially designed collision chamber[12] to extract low energy ions. This field introduces an additional uncertainty in the energy of interaction. Relative cross sections are well reproduced, and we estimate that the absolute cross sections reported are accurate to a factor of 2.

III. THEORETICAL

A key problem in obtaining information from measurements such as those made in the present study is an accurate determination of the true microscopic cross section for reaction, $\sigma(E)$. It has been shown that direct deconvolution of the phenomenological cross section measured does not yield a unique reaction cross section independent of the experimental energy distributions.[19] Thus, a choice for the form of $\sigma(E)$ must be made and eventually shown to be consistent with the data by averaging over the experimental conditions (as above).[16] This choice, however, is not an easy one. No *ab initio* theory presently exists which derives the correct general form for particle transfer reactions. While trajectory calculations[20] can yield $\sigma(E)$ for a given reaction, this is clearly of no general help to the experimentalist. Simple models,[21] such as hard-sphere cross sections, line of centers cross sections, or cross sections determined by the long-range portion of the interaction potential of the reactants, may be used. However, these are primarily useful in defining an encounter but not subsequent events which may or may not lead to reaction.

In the past, workers have assumed forms for $\sigma(E)$ which are easy to handle mathematically, such as step functions,[22] linear functions,[12,22,23] and exponential functions.[24]

Another approach is to "derive" $\sigma(E)$ from statistical considerations developed for understanding reaction rates such as transition state theory,[25] RRKM theory,[26] and phase space theory.[27,28] However, these theories were developed such that no particlar form for the reaction cross section need be assumed. Consequently, additional assumptions are required to derive a cross section.[25,29,30]

A. Form for $\sigma(E)$

The choice we will make for the reaction cross sections is that it has the general form

$$\sigma(E) \propto \left(\frac{E - E_0}{E}\right)^n \qquad (8)$$

when we refer to a direct state to state reaction. Here, the reactants have a total energy E and the barrier to reaction is E_0. When $n = 1$, this form reduces to the familiar line of centers model which has often been found to have approximately the correct shape for experimental cross sections.[21] Expression (8) is also familiar as the probability derived by Kassel[31] for one particular oscillator out of a system of $n+1$ oscillators to have an energy greater than E_0 when the total system energy is E. We expect that the problem of determining whether sufficient energy is in a reaction coordinate of a system having $n+1$ degrees of freedom should be related. The form of (8) can also be viewed as a ratio of numbers of states (in a classical approximation)[26] of a transition state to that of an energized molecule[25] or as the ratio of flux in the reaction product channel relative to the incident flux.[32,33]

This latter viewpoint suggests several possible refinements which may become warranted as more experiments are done and compared with theory. The first of these refinements is to simply replace (8) by the ratio

$$\sigma(E) \propto N^*(E^*)/N(E) , \qquad (9)$$

where $N(x)$ is the number of quantum states of a system with an energy less than or equal to x, $N^*(E^*)$ refers to a transition state with $E^* = E - E_0$, and $N(E)$, for a direct reaction, refers to the reactants. Now, rather than use classical approximations yielding the form in (8), other means of counting states, such as direct count or semiclassical expressions,[26] may be utilized. These may be more accurate especially near reaction threshold. It can also be noted that expression (9), using a classical approximation, may yield

$$\sigma(E) \propto (E - E_0)^n/E^m \qquad (10)$$

such that n and m are not equal. This could be the case, for instance, if a tight transition state were involved.[34]

The second refinement is the extension to reactions which may proceed via long-lived complex formation. The cross section for reaction is now related to

$$\sigma^\alpha(E) \propto \frac{N^\alpha(E)}{\sum_\alpha N^\alpha(E)} , \tag{11}$$

where the sum is over all decomposition paths, designated by α, of the complex (including back to reactants).[34] The expressions (9) and (11) can be identified with the reaction probabilities of Miller's unified statistical theory[33] and thus may be extended to intermediate cases between direct and complex mechanisms.

B. Influence of product dissociation on the form for $\sigma(E)$

The possibility of product dissociation can have a profound influence on the cross section observed for product formation. The thermodynamic threshold for such dissociation is simply the dissociation energy of the bond broken during reaction. However, not all of the available energy will be in the internal modes of the appropriate product. We can estimate that energy assuming that the energy is statistically distributed among the degrees of freedom of the products.[34,35] Treating the problem classically, neglecting angular momentum,[36] and remembering that only n internal modes are "active" (excluding the reaction coordinate), it can be shown that the probability of an energy greater than E_V is in internal modes of the products at a total available energy $(E - E_0)$ is just

$$P = [E_V/(E - E_0)]^n . \tag{12}$$

We now assume the product ion dissociates if its internal energy exceeds its bond dissociation energy, D. We define the parameter a as the average fraction of internal energy E_V in the ionic fragment. The dissociation probability (i.e., the probability $aE_V \geqslant D$) becomes

$$P = [D/a(E - E_0)]^n . \tag{13}$$

If the neutral product is monatomic, a equals unity,[37] and if polyatomic, $0 < a < 1$.

C. Expression to be used for $\sigma(E)$

If we recognize that expression (8) is the reaction probability, P_r, the final result for $\sigma(E)$ is given by

$$\sigma(E) = 2\pi \int_0^{b_m} P_r b\, db , \tag{14}$$

where b is the collision impact parameter and b_m is the maximum value of b for which reaction occurs.[21] Thus, we find

$$\sigma(E) = \pi b_m^2 P_r = \sigma_0 P_r . \tag{15}$$

The value of σ_0 may be determined by assuming one of two simple models: one based on the long-range intermolecular potential of the reactants[38] and the hard-sphere model.[21] The long-range intermolecular potential is given by $-C/r^s$, where r is the distance between reactants. For the specific case of ion–molecule reactions, $(s = 4, C = \frac{1}{2}\alpha$, α is the polarizability of the neutral reactant), the result is

$$\sigma_0 = \pi e(2\alpha/E)^{1/2} . \tag{16}$$

This should only be the case until $E = 2\alpha/d^4$, where d is

the hard-sphere radius.[8] Above this energy, usually less than 1 eV, $\sigma_0 = \pi d^2$, the hard-sphere model result.

Summarizing, the form for the reaction cross section below E_0 is zero. For $E_0 < E < E_0 + D/a$, $\sigma(E)$ is given by

$$\sigma(E) = \sigma_0 \left(\frac{E - E_0}{E}\right)^n \tag{17}$$

For $E > E_0 + D/a$, the cross section is the product of Eqs. (13) and (17) or simply

$$\sigma(E) = \sigma_0 (D/aE)^n . \tag{18}$$

D. Application to experiment

For the reactions in the present study, the total energy E is taken equal to the relative translation energy since under our experimental conditions this energy is much greater than the internal energy of the reactants. We also assume that there is no barrier for reverse reaction (i.e., the transition state is loose). Consequently, E_0 represents the energy difference between products and reactants. We use Eqs. (17) and (18) to fit the data treating σ_0, E_0, n and a as variable parameters. [Note that $D = D^0$ (neutral reactant bond) $- E_0$.] Determination of these parameters is aided by several techniques of analysis. First, n can be determined from a log–log plot of σ vs E since the slope of this plot at high energies (after product dissociation commences) is $-n$. In general, we restrict ourselves to integral and half-integral values of n. Knowing n, σ_0, and E_0 may be determined by plotting $\sigma^{1/n} E$ vs E for low energies which gives a slope of $\sigma_0^{1/n}$ and an energy axis intercept of E_0. The parameter a is determined by fitting the high side of the excitation function. An alternate means of assessing n and E_0 is to plot $\sigma/[E(\partial\sigma/\partial E)]$ vs E for low energies, which gives an energy axis intercept of E_0 and a slope of $1/nE_0$. Having determined n and approximate values of σ_0 and E_0, we convolute this starting function as discussed above and adjust these parameters until a good fit is obtained. We also assess how sensitive the fit is to the value of n which fits the best. Often, within experimental error, several sets of parameters fit the data equally well. This, then is how the errors in E_0 are determined.

IV. RESULTS

A. $Co^+ + C_2H_4$

Cobalt ions react with ethene to yield two products, CoH^+, Reaction (1), and $CoCH_2^+$, Reaction (2). Variation of cross section with relative kinetic energy is shown in Figs. 3 and 4, respectively. The background at low energies in Fig. 3 is apparently due to a contribution from reaction at higher energies outside the collision chamber. The theoretical fit shown in Fig. 3 is obtained using only Eq. (17) with $n = 2$, $\sigma_0 = 1.81$ Å^2, and $E_0 = 2.5$ eV. An equally good fit is obtained with n as low as 1.5 and as high as 3.0 giving threshold energies from 2.9 to 2.0 eV. The sharp rise in cross section at ~ 18 eV in Fig. 3 is possibly an indication of a new product channel, perhaps due to formation of electronically excited CoH^+ or C_2H_3.

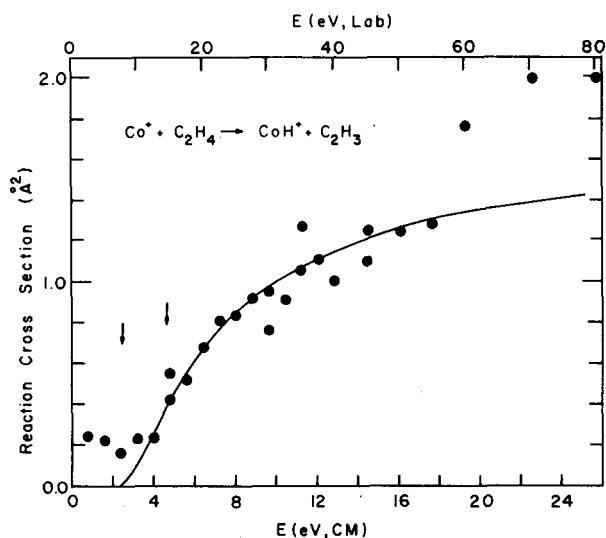The data shown in Fig. 4 for Reaction (2) are best fit

FIG. 3. Variation in experimental cross section with relative kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale) for Reaction (1). Arrows indicate the threshold energy for reaction, 2.5 eV, and the lower limit on the H−C_2H_3 bond energy, 4.68 eV. The curve is the fit to the data given in the text convoluted as discussed.

using $n = 5$, $\sigma_0 = 18.6$ Å^2, $E_0 = 3.8$ eV, and $a = 0.80$. The data are also fit reasonably well if $n = 6$ or 4 corresponding to thresholds of 3.5 and 4.1 eV, respectively. The background at low energies is believed to be much less than for process (1) since here reaction occurs over a much narrower energy range.

B. Co$^+$ + c-C$_3$H$_6$

While other products are also observed, the primary reaction of cobalt ions and cyclopropane is formation of the metal carbene ion, Reaction (3). A crude energy analysis gives the laboratory energy of this product as 1.54 ± 0.80 eV when $E_{1ab}(Co^+) = 3.70 \pm 0.75$ eV and as 0.83
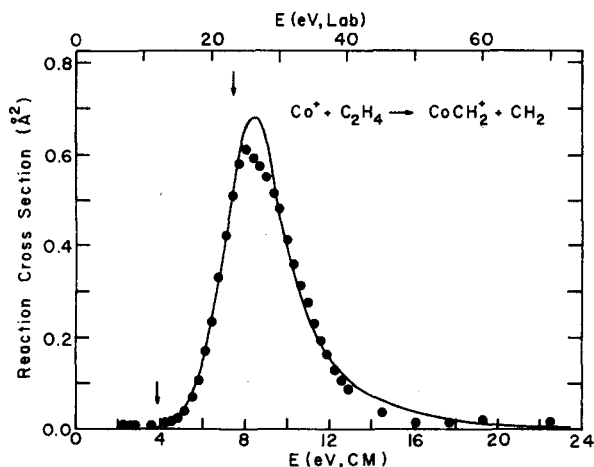

FIG. 4. Variation in experimental cross section with relative kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale) for Reaction (2). Arrows indicate the threshold energy for reaction, 3.8 eV, and the carbon−carbon bond energy of ethene, 7.47 eV. The curve is the fit to the data given in the text convoluted as discussed.

± 0.43 eV when $E_{1ab}(Co^+) = 1.5 \pm 0.75$ eV. In both cases, these energies are sufficiently low to suggest the CoCH$_2^+$ ion has the velocity of the center of mass, rather than a velocity resulting from a direct reaction. The former possibility corresponds to CoCH$_2^+$ energies of 1.56 and 0.63 eV, respectively, while a spectator stripping model[39] predicts 3.0 and 1.2 eV. This observation conforms with the notion that a long-lived intermediate, a metallocyclobutane, is formed.

The excitation function shown in Fig. 5 cannot be fit using Eq. (17). This may be due to the influence of the long-lived intermediate, especially since metallocyclobutanes have been postulated as intermediates in the isomerization of cyclopropanes to alkenes.[40] In our particular case, rearrangement of cyclopropane to propene

$$Co^+ + c\text{-}C_3H_6 \rightarrow Co^+ + C_3H_6 \qquad (19)$$

is exothermic by 7.8 kcal/mol.[41] In our experiment, we have no means of monitoring such a reaction. The influence this possibility may have on the cross section for Reaction (3) is unknown. The fit shown in Fig. 5 utilizes expression (10) for the reaction probability. The parameters used are $n = 3.5$, $m = 5.0$, $\sigma_0 = 46.3$ Å^2 (eV)$^{3/2}$, $E_0 = 0.5$ eV, and $a = 0.60$.

Other products noted are CoC$_2$H$_4^+$, CoC$_2$H$_2^+$, CoC$_3$H$_4^+$, C$_3$H$_5^+$, and the adduct, CoC$_3$H$_6^+$. All but the latter are formed in highly endothermic reactions. Since they cumulatively account for less than 10% of the product yield, no good excitation function data could be obtained for them. The adduct is a collisionally stabilized complex as established by the pressure dependence of its cross section.

C. Co$^+$ + c-C$_2$H$_4$O

The reaction of cobalt ions with ethylene oxide forms a variety of products, Fig. 6. All of these find analogy
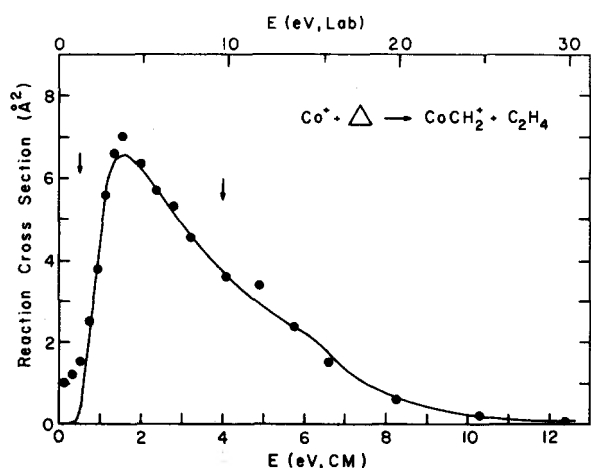

FIG. 5. Variation in experimental cross section with relative kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale) for Reaction (3). Arrows indicate the reaction threshold at 0.5 eV and the energy needed to produce methylene and ethene from cyclopropane, 4.0 eV. The curve is the fit to the data given in the text convoluted as discussed. The inflection point at about 6 eV marks the energy at which product dissociation begins according to the model outlined in the text.

with the products observed in the cyclopropane system. For present purposes, however, we need only consider the cross section for formation of $CoCH_2^+$. It is observed to decrease monotonically with increasing energy and is considerably larger than the cross sections measured in the other two systems. This clearly indicates that Reaction (4) is exothermic. The other major product of an exothermic reaction in this system is $CoCO^+$, which probably results from the rearrangement of ethylene oxide to acetaldehyde followed by decomposition of the latter species.[42] The same product is observed in the reaction of Co^+ with acetaldehyde, where the carbene product is not detected.[43]

V. DISCUSSION

The test of any model is, of course, whether it explains what is observed. It can be seen that for our proposed cross section this is true not just at threshold but throughout the energy range. A more severe test, however, is that the parameters used in obtaining these fits be physically meaningful. This is especially true of E_0 since we would like to extract thermochemical information from our experiments. The thermochemical data inferred from this study are summarized in Table I. The cobalt hydride dissociation energy of $> 2.2 \pm 0.3$ eV (the limit is due to the poorly known C–H bond energy of ethene) compares well with the value 2.3 ± 0.2 eV determined from the endothermic reaction of Co^+ with hydrogen.[44] The agreement between the thermochemical data measured for Reactions (2), (3), and (4) is also good. The observation that a straightforward interpretation of the data for Reaction (2) yields a bond energy which agrees with limits established by Reactions (3) and (4)

TABLE I. Thermochemical data.

Species	$\Delta H^0_{f\ 298}$ (kcal/mol)	Reference
CH_2	92.4 ± 1.0	a
C_2H_4	12.54 ± 0.07	b
$c\text{-}C_3H_6$	12.73 ± 0.14	c
CH_2O	-25.95 ± 0.12	c
$c\text{-}C_2H_4O$	-12.58 ± 0.15	b
	D^0_{298} (kcal/mol)	
$H\text{-}C_2H_3$	$> 108 \pm 2$	d
$Co^+\text{-}H$	52 ± 4	e
	$> 50 \pm 10$	This work [Reaction (1)]f
$Co^+\text{-}CH_2$	85 ± 7	This work [Reaction (2)]f
	$< 92 \pm 1 (81 \pm 7)$	This work [Reaction (3)]f
	$> 79 \pm 1$	This work [Reaction (4)]

aJANAF Thermochemical Tables, 1975 Supplement, J. Phys. Chem. Ref. Data 4 (1975).
bJANAF Thermochemical Tables, Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. 37 (1971).
cJ. D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds (Academic, New York, 1970).
dD. M. Golden and S. W. Benson, Chem. Rev. 69, 125 (1969).
eReference 44.
fCalculated from the difference between the dissociation energy of the neutral bond broken and the measured endothermicity (listed in text).

gives us confidence that this method is a useful means for interpreting the data. While the bond energy derived from Reaction (3) is in good accord, 3.5 ± 0.3 eV, the interpretation of this reaction was not straightforward. We therefore choose the result from Reaction (2), $D^0(Co^+\text{-}CH_2) = 3.7 \pm 0.3$ eV, as the best value. This bond energy is in the same range as limits by other experimental means for $D^0(Mn^+\text{-}CH_2)$ of 4.0 to 4.3 eV and $D^0[(CO)_5Mn^+\text{-}CH_2] = 3.3$ eV.[7]

Values for the other parameters used to interpret the experimental results also seem reasonable. Certainly, the effective cross sections, σ_0, are on the order of hard-sphere interactions. The assumption that such hard-sphere cross sections will remain nearly constant over the energy range examined should be good.[45] The observation that the σ_0's used to interpret Reactions (1) and (2) are different is consistent with our assumption that these reactions are direct and do not proceed through a common intermediate. The inclusion of the long-range ion-induced dipole interaction into σ_0 [Eq. (16)] could help explain the behavior observed for Reaction (3) at the lowest energies.

The values for parameter a can be understood qualitatively by noting whether the product ion or neutral is likely to have lower vibrational frequencies and thus a higher density of states. For Reaction (2), the ionic product would be expected to have lower energy modes, and a is correspondingly found to be high, 0.8. The vibrational frequency of CoH^+ is undoubtedly much higher than those of C_2H_3. Consequently, little excitation of this ionic product would be predicted. Since the cross section for production of CoH^+, Reaction (1), is observed to increase monotonically from threshold, we take the value of a to be quite low. In Reaction (3), both the ionic
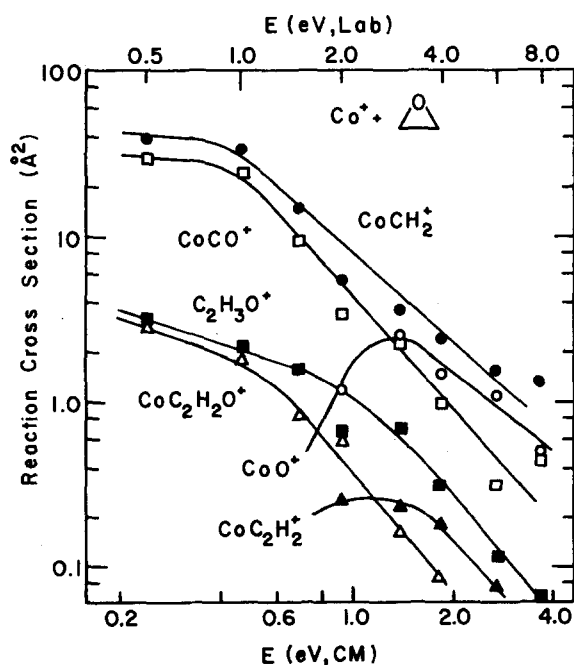

FIG. 6. Variation in experimental cross section with relative kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale) for reaction of Co^+ with ethylene oxide. Lines through the data are drawn as an aid to the reader and have no theoretical significance.

and neutral products have two heavy atoms. Therefore, it should be an intermediate case, and indeed, a is found to be 0.6.

The identification of expression (8) as a ratio of numbers of states in a classical approximation suggests that n should correspond to the degrees of freedom of the reactants, collision complex, or products. The values of n used above are generally much less than the total number of oscillators involved. This is perhaps to be expected since for a direct process it is not clear whether any mixing of energy among modes should occur. However, this extreme assumption seems unrealistic. While not expected to be completely statistical, extensive energy may flow between strongly coupled modes of a collision complex, however short-lived. It should be cautioned that regarding n as related to the degrees of freedom is only true in the limit of a classical approximation. It was observed in the early applications of expression (8) to unimolecular decomposition rates that $n+1$ was often half the total number of oscillators.[46] More sophisticated treatments for the numbers of states has led to the conclusion that all oscillators are, in fact, active. Whether this will also be the case for direct endothermic bimolecular reactions, a system well removed from an equilibrium situation, will require further study.

VI. CONCLUSION

A form has been proposed for the energy dependence of reaction cross sections which draws extensively from ideas formulated to examine reaction rates. Utilization of this form gives good agreement with data for endothermic bimolecular reactions including the energy region where product dissociation affects the observed cross section. Values of the parameters used to fit the data seem reasonable. Most important, energy thresholds for the reactions observed are substantiated by thermochemical data from other sources. This means of interpretation has allowed us to determine the bond energy for the cobalt carbene ion, $D^0(Co^+-CH_2) = 3.7 \pm 0.3$ eV.

The cobalt carbene ion bond is significantly stronger than the cobalt methyl ion bond, $D^0(Co^+-CH_3) = 2.65 \pm 0.17$ eV.[44] Substantial π bonding would appear to contribute to this difference. Calculations on $NiCH_2$ and $NiCH_3$ lead to the conclusion that only a weak π bond exists for the former species.[47] Contraction of the metal d orbitals due to a positive charge will likely change the π-bonding characteristics as will specifics of the electronic structure of the cobalt carbene ion. Generalized valence bond considerations predict a $^3\Sigma$ ground state for the isoelectronic CoO^+ which does not correlate with ground state separated species.[48] Since coupling of ground state $Co^+(^3F)$ with ground state $CH_2(^3B_1)$ gives rise to several states which may cross the potential energy curves arising from higher levels of Co^+ and CH_2, the electronic structure of $CoCH_2^+$ is unclear. Ab initio calculations on this system will be of interest now that experimental numbers are available.

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