Conversion of CH₄ to CH₃OH: Reactions of CoO⁺ with CH₄ and D₂, Co⁺ with CH₃OD and D₂O, and Co⁺(CH₃OD) with Xe

Yu-Min Chen, D. E. Clemmer, and P. B. Armentrout

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received January 18, 1994. Revised Manuscript Received April 25, 1994

Abstract: The mechanisms and energetics involved in the conversion of CH₄ to CH₃OH by CoO⁺ are examined by using guided ion beam mass spectrometry. The forward and reverse reactions, CoO⁺ + CH₄ = Co⁺ + CH₃OH, the collisional activation of Co⁺(CH₃OH), and the related reactions, CoO⁺ + D₂ = Co⁺ + D₂0, are studied. It is found that the oxidations of methane and D₂ by CoO⁺; both exothermic reactions, do not occur until overcoming activation barriers of 0.56 ± 0.08 and 0.75 ± 0.04 eV, respectively. The behavior of the forward and reverse reactions in both systems is consistent with reactions that proceed via the insertion intermediates R-Co⁺-OH, where R = CH₃ or H. The barrier is probably attributable to a four transition state associated with addition of RH across the CoO⁺ bond. In the Co⁺ + CH₃OH system (where CH₃OD labeled reactant is used), reactions explained by initial C-H and O-H activation are also observed. The reaction mechanisms and potential energy surfaces for these systems are derived and discussed. Phase space theory calculations are used to help verify these details for the CoO⁺ + D₂ system. Thermochemistry for several species including CoOH⁺, Co⁺, COH, CoCH₃⁺, Co⁺(CH₃OD), COOCH₃⁺, and possibly OCoCH₃⁺ is derived from measurements of reaction thresholds.

Introduction

The direct conversion of methane to methanol has been studied for more than a half century because of its great economic and scientific importance. Although this oxidation reaction,

\[ CH₄ + 1/2 O₂ \rightarrow CH₃OH \quad ΔH_{298} = -1.32 \text{ eV} (1) \]

is thermodynamically favored, the best catalyst at present provides a yield of only about 8%. Catalytic conversion of CH₄ to CH₃OH has become an active research area with the search for a more efficient catalyst listed as one of ten challenges for catalysis.

One means of providing fundamental information regarding this process is to study a prototypical gas-phase reaction

\[ MO⁺ + CH₄ \rightarrow CH₃OH + M⁺ \quad (2) \]

Such studies can potentially provide quantitative information regarding the thermodynamics and mechanisms for this process, while simultaneously examining the periodic trends in the chemistry. At present, only a few gas-phase studies of reaction 2 have been made. Schröder and Schwarz reported a Fourier transform ion cyclotron resonance (FTICR) study of the reaction of FeO⁺ with CH₄. At thermal energies, the reaction produces 57% of FeOH⁺ + CH₃, 2% of FeCH₃⁺ + H₂O, and 41% of Fe⁺ + CH₃OH, which were explained by a reaction mechanism involving a CH₃-Fe⁺OH intermediate. Additional experimental and theoretical studies of various possible intermediates were later conducted as well.

In a recent paper on the reactions of ScO⁺, TiO⁺, and VO⁺ with D₂, we suggested that there should be two main criteria in evaluating the efficiency of reaction 2. First, reaction 2 should be exothermic or thermoneutral. Because the reaction, O⁺ + CH₄ = CH₃OH, has an exothermicity of -3.846 ± 0.005 eV, Table 1, reaction 2 will be endothermic for any MO⁺ with a bond stronger than 3.85 eV, such as ScO⁺, TiO⁺, or VO⁺, but no other first-row transition-metal ion oxide. Second, MO⁺ should have a suitable electron configuration such that reaction 2 conserves spin. As discussed elsewhere, CoO⁺ is a promising candidate for efficient conversion of CH₄ to CH₃OH. The 0 K bond energy of Co⁺-O is 3.25 ± 0.05 eV, so reaction 3 is thermodynamically favored.

\[ CoO⁺ + CH₄ \rightarrow Co⁺ + CH₃OH \quad ΔH_0 = -0.60 \pm 0.05 \text{ eV} (3) \]

Further, it was suggested that CoO⁺ has a suitable electron configuration to activate CH₄, and that reaction 3 is spin allowed.

In this paper, we examine the energetics and mechanism of reaction 3 in both the forward and reverse directions, as well as probing how one of its intermediates, Co⁺(CH₃OH), decomposes when activated by collisions with Xe. We also study the related but simpler interaction of CoO⁺ with D₂ and its reverse, a reaction that has been briefly studied at thermal energies by Schröder et al. We are able to determine a fairly detailed picture of the potential energy surfaces of these reactions and find in both systems that a reaction barrier restricts the oxidation process and its reverse. These conclusions lead to a more careful assessment
Table 1. Bond Energies and Enthalpies of Formation at 0 K

<table>
<thead>
<tr>
<th>species</th>
<th>( \Delta H^\circ (eV) )</th>
<th>( \Delta H^\circ (eV) )</th>
<th>( D_0 (eV) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>2.558(0.001)</td>
<td>Co(^{17})O</td>
<td>3.25(0.05)</td>
</tr>
<tr>
<td>H</td>
<td>2.339</td>
<td>Co(^{18})O</td>
<td>1.98(0.06)</td>
</tr>
<tr>
<td>D</td>
<td>2.278</td>
<td>Co(^{17})D</td>
<td>2.01(0.06)</td>
</tr>
<tr>
<td>OH</td>
<td>0.405(0.003)</td>
<td>Co(^{17})OH</td>
<td>1.86(0.05)</td>
</tr>
<tr>
<td>OD</td>
<td>0.382(0.001)</td>
<td>Co(^{18})D</td>
<td>3.13(0.04)</td>
</tr>
<tr>
<td>CH(_2)</td>
<td>4.02(0.03)</td>
<td>Co(^{18})CH(_2)</td>
<td>3.29(0.05)</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>1.553(0.004)</td>
<td>Co(^{17})CH(_3)</td>
<td>2.10(0.04)</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>-2.476(0.001)</td>
<td>Co(^{18})H(_2)O</td>
<td>1.67(0.06)</td>
</tr>
<tr>
<td>HDO</td>
<td>-2.513(0.001)</td>
<td>Co(^{17})OCH(_3)</td>
<td>2.0(0.3)</td>
</tr>
<tr>
<td>CH(_2)O</td>
<td>-1.086(0.005)</td>
<td>Co(^{17})CH(_2)O</td>
<td>2.23(0.05)</td>
</tr>
<tr>
<td>CH(_3)O</td>
<td>-0.012(0.01)</td>
<td>Co(^{17})OCH(_3)</td>
<td>1.53(0.08)</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>0.25(0.04)</td>
<td>Co(^{17})OCH(_3)</td>
<td>2.0(0.3)</td>
</tr>
<tr>
<td>CH(_2)OH</td>
<td>-1.767(0.03)</td>
<td>Co(^{17})CH(_2)OH</td>
<td>2.23(0.05)</td>
</tr>
<tr>
<td>CH(_3)OD</td>
<td>-2.005(0.003)</td>
<td>Co(^{17})OCH(_3)OD</td>
<td>2.0(0.3)</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>-0.688(0.004)</td>
<td>Co(^{17})OCH(_3)</td>
<td>2.0(0.3)</td>
</tr>
</tbody>
</table>


of the ground-state electron configuration for Co\(^{17}\)O and its suitability for activation of CH\(_4\).

Experimental Section

General Procedures. The guided ion beam instrument on which these experiments have been performed has been described in detail previously.\(^{11,12}\) Ions are created in a flow tube source, described below. The ions are extracted from the source, accelerated, and focused into a magnetic sector momentum analyzer for mass analysis. Mass-selected ions are slowed by a radial trap and focused into a quadrupole mass filter for mass analysis. Mass-selected ions are then detected. Ion intensities are converted to absolute values in ref 37 and footnote k.

where \( E \) is the relative kinetic energy of the ions, \( E_0 \) is the 0 K reaction threshold, \( \sigma \) is an energy-independent scaling factor, and \( n \) is an adjustable parameter. Equation 4 takes into account the thermal internal energy of the reactants by treating the calculated cross section as a sum over vibrational states (with energies \( E_v \) and populations \( g_v \)) as described previously,\(^{13,14}\) and by including the thermal rotational energy. In this study, the vibrational energies of \( D_2, CH_4 \), and \( Co^{17}O \) at 298 K are negligible; only the vibrational energies of \( CH_3OD \) and \( Co^{17}CH_3OD \) were included in eq 4. The vibrational frequencies of \( CH_3OD \) were taken from Shimanochi.\(^{23}\) No vibrational frequencies are available for \( Co^{17}CH_3OD \), so we estimated these frequencies as the vibrational frequencies of \( CH_3OD \) plus three cobalt-methanol vibrational frequencies (one stretching and two bending) of 330, 192, and 106 cm\(^{-1}\). The total rotational energy of the reactants at 298 K is \( E_{rot} = 3k_B T/2 = 0.039 \) eV for the \( Co^{17} + D_2, Co^{17} + CH_4, \) and \( Co^{17}CH_3OD + Xe \) systems, \( 2k_B T = 0.053 \) eV for the \( Co^{17} + D_2 \) system, and \( 5k_B T/2 = 0.066 \) eV for the \( Co^{17}CH_3 + CH_4 \) system. Before comparison with the data, eq 4 must be convoluted over the rotational and electronic energy distributions, as described previously.\(^{13,14}\)

(16) Haynes, C. L.; Armentrout, P. B. Organometallics, accepted for publication.
(26) These three frequencies were estimated from a theoretical calculation for \( Mg^{17} \)(CH3OD): Sudopla, M.; Bauschlicher, C. W. J. Chem. Phys. Lett. 1992, 199, 215.
(27) The stretching mode of 415 cm\(^{-1}\) was scaled to 330 cm\(^{-1}\) by using a Morse potential model, and the two bending mode frequencies were used without modification. Variation of these frequencies by ±30% has no significant effect on the threshold analysis.
Rh(I)-Catalyzed Olefin Hydroboration Reaction

TS, and SOT stand for equilibrium, transition state, and second order top geometries, with parentheses indicating that one of the estimated imaginary frequencies is not related to the reaction.

Figure 1. The critical structures of the L1A mechanism of the reaction HB(OH)₂ + C₂H₄ → C₂H₄B(OH)₂. EQ, TS, and SOT stand for equilibrium, transition state, and second order top geometries, with parentheses indicating that one of the estimated imaginary frequencies is not related to the reaction.

Figure 2. The critical structures of the L1B mechanism of the reaction HB(OH)₂ + C₂H₄ → C₂H₄B(OH)₂. See Table 1 for notation.

highly unfavorable. In order to find the origin of the small binding energy, we divide this binding energy \( \Delta E \) into three parts:

\[
\Delta E = \text{DEF(a1)} + \text{DEF(C₂H₄)} + \text{INT}
\]  

DEFs are energies required to deform the reactant fragments, a1 and C₂H₄, from their respective equilibrium geometries to the geometries in the product complex a2. INT is the interaction energy between the deformed fragments. Table 3 shows that the energy required to open the narrowest angle of Y to make it a T shape is extremely large (66 kcal/mol), compared to those required to open the wider angle for Y to make a T to be discussed later with the product a16 and a19. Since the product a2 is a metallocycle, the interaction energy INT is large in magnitude but cannot compensate the large DEF.

The reaction proceeds further via migratory insertion of the C=C bond into the Rh-H bond through TS (a3), which is an early transition state, in accord with high exothermicity of the a2 → a3 → a4 process. Table 2 shows that the Rh-H bond in a3 is only 0.045 Å longer than in a2, and the C=C distance has not changed. Although the C¹-H distance in a3 is 0.7 Å shorter than in a2, it is still very far from the regular C-H bond length. The Rh-C¹ distance is lengthened by about 0.1 Å in a3, but the bond is still preserved in the TS. Geometry of the reacting fragment has a double three-centered character, with H, C¹, and C² all interacting with Rh. The barrier height is 6.5 kcal/mol relative to a2, and a3 lies substantially below the initial reactants, RhCl(Ph₃)₂ + HB(OH)₂ + C₂H₄ (a0).

Insertion maintaining C₆ symmetry results in the complex a4. RhCl(Ph₃)₂[B(OH)₂]C₆H₆, which is 28.2 kcal/mol lower than

\[
\text{DEF(a1)} = \text{DEF(C₂H₄)} + \text{INT}
\]  

where X is the center of the C=C bond, are in the range of 90°–100°. The Rh-H and Rh-B bond lengths are elongated by about 0.1 Å, relative to the free C₂H₄ molecule and close to those in metallocycle structures. The Rh-C¹ and Rh-C² distances are 2.124 and 2.161 Å, respectively, which also are close to those for Rh-C covalent bond. Thus, a2 has a metallocycle structure.

The binding energy Rh(H)Cl(Ph₃)₂[B(OH)₂]C₂H₄ (a2) → RhCl(Ph₃)₂[B(OH)₂] + C₂H₄ is calculated to be only 0.1 kcal/mol, a surprising small value. The reason of this is that the attack of the C₂H₄ to Rh(H)Cl(PH₃)₂[B(OH)₂] is six-coordinated and has nearly an octahedral geometry of the reacting fragment has a double three-centered character, with H, C¹, and C² all interacting with Rh. The barrier height is 6.5 kcal/mol relative to a2, and a3 lies substantially below the initial reactants, RhCl(Ph₃)₂ + HB(OH)₂ + C₂H₄ (a0).

Insertion maintaining C₆ symmetry results in the complex a4. RhCl(Ph₃)₂[B(OH)₂]C₆H₆, which is 28.2 kcal/mol lower than

\[
\text{DEF(a1)} = \text{DEF(C₂H₄)} + \text{INT}
\]  

where X is the center of the C=C bond, are in the range of 90°–100°. The Rh-H and Rh-B bond lengths are elongated by about 0.1 Å, relative to the free C₂H₄ molecule and close to those in metallocycle structures. The Rh-C¹ and Rh-C² distances are 2.124 and 2.161 Å, respectively, which also are close to those for Rh-C covalent bond. Thus, a2 has a metallocycle structure.

The binding energy Rh(H)Cl(Ph₃)₂[B(OH)₂]C₂H₄ (a2) → RhCl(Ph₃)₂[B(OH)₂] + C₂H₄ is calculated to be only 0.1 kcal/mol, a surprising small value. The reason of this is that the attack of the C₂H₄ to Rh(H)Cl(PH₃)₂[B(OH)₂] is six-coordinated and has nearly an octahedral geometry of the reacting fragment has a double three-centered character, with H, C¹, and C² all interacting with Rh. The barrier height is 6.5 kcal/mol relative to a2, and a3 lies substantially below the initial reactants, RhCl(Ph₃)₂ + HB(OH)₂ + C₂H₄ (a0).

Insertion maintaining C₆ symmetry results in the complex a4. RhCl(Ph₃)₂[B(OH)₂]C₆H₆, which is 28.2 kcal/mol lower than

\[
\text{DEF(a1)} = \text{DEF(C₂H₄)} + \text{INT}
\]  

where X is the center of the C=C bond, are in the range of 90°–100°. The Rh-H and Rh-B bond lengths are elongated by about 0.1 Å, relative to the free C₂H₄ molecule and close to those in metallocycle structures. The Rh-C¹ and Rh-C² distances are 2.124 and 2.161 Å, respectively, which also are close to those for Rh-C covalent bond. Thus, a2 has a metallocycle structure.

The binding energy Rh(H)Cl(Ph₃)₂[B(OH)₂]C₂H₄ (a2) → RhCl(Ph₃)₂[B(OH)₂] + C₂H₄ is calculated to be only 0.1 kcal/mol, a surprising small value. The reason of this is that the attack of the C₂H₄ to Rh(H)Cl(PH₃)₂[B(OH)₂] is six-coordinated and has nearly an octahedral geometry of the reacting fragment has a double three-centered character, with H, C¹, and C² all interacting with Rh. The barrier height is 6.5 kcal/mol relative to a2, and a3 lies substantially below the initial reactants, RhCl(Ph₃)₂ + HB(OH)₂ + C₂H₄ (a0).

Insertion maintaining C₆ symmetry results in the complex a4. RhCl(Ph₃)₂[B(OH)₂]C₆H₆, which is 28.2 kcal/mol lower than
Table 2. Summary of Fitting Parameters of Eq 4 Used to Model Reaction Cross Sections

<table>
<thead>
<tr>
<th>Reactions</th>
<th>σ0</th>
<th>n</th>
<th>Ef</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co⁺ + D₂O → CoD⁺ + OD</td>
<td>0.86(0.08)</td>
<td>1.2(0.1)</td>
<td>3.16(0.05)</td>
</tr>
<tr>
<td>Co⁺ + OD + D</td>
<td>0.11(0.03)</td>
<td>1.8(0.3)</td>
<td>2.11(0.12)</td>
</tr>
<tr>
<td>CoO⁺ + D₂</td>
<td>1.62(0.13)</td>
<td>2.1(0.2)</td>
<td>0.75(0.04)</td>
</tr>
<tr>
<td>Co⁺ + D₂O + D</td>
<td>0.20(0.05)</td>
<td>1.9(0.2)</td>
<td>0.60(0.15)</td>
</tr>
<tr>
<td>Co⁺ + [O + D₂]</td>
<td>1.96(0.15)</td>
<td>0.9(0.1)</td>
<td>3.32(0.09)</td>
</tr>
<tr>
<td>Co⁺ + OD + D</td>
<td>0.12(0.04)</td>
<td>1.9(0.2)</td>
<td>1.46(0.13)</td>
</tr>
<tr>
<td>Co⁺ + CH₃OD + CH₃</td>
<td>2.99(0.12)</td>
<td>1.1(0.2)</td>
<td>0.81(0.04)</td>
</tr>
<tr>
<td>Co⁺ + CH₃OD + CH₄</td>
<td>1.10(0.19)</td>
<td>1.9(0.2)</td>
<td>1.84(0.08)</td>
</tr>
<tr>
<td>Co⁺ + CH₃OD + DOH</td>
<td>1.06(0.12)</td>
<td>1.4(0.2)</td>
<td>1.89(0.06)</td>
</tr>
<tr>
<td>Co⁺ + CH₃OD + CH₃OH</td>
<td>0.73(0.10)</td>
<td>1.0(0.1)</td>
<td>1.212</td>
</tr>
<tr>
<td>Co⁺ + CH₃OD + CH₄</td>
<td>0.19(0.04)</td>
<td>1.5(0.2)</td>
<td>2.38(0.12)</td>
</tr>
<tr>
<td>Co⁺ + CH₃OD + DOH</td>
<td>0.06(0.02)</td>
<td>2.0(0.2)</td>
<td>0.90(0.08)</td>
</tr>
<tr>
<td>Co⁺ + CH₃OD + CH₄</td>
<td>0.46(0.05)</td>
<td>1.7(0.1)</td>
<td>0.56(0.08)</td>
</tr>
<tr>
<td>Co⁺ + CH₃OD + CH₄</td>
<td>0.05(0.02)</td>
<td>2.6(0.2)</td>
<td>0.56(0.08)</td>
</tr>
<tr>
<td>Co⁺ + [O + CH₄]</td>
<td>0.53(0.16)</td>
<td>1.4(0.2)</td>
<td>3.29(0.07)</td>
</tr>
<tr>
<td>Co⁺ + [O + CH₄] + H + H</td>
<td>0.20(0.05)</td>
<td>1.7(0.2)</td>
<td>2.66(0.12)</td>
</tr>
<tr>
<td>Co⁺ + [O + CH₄] + H</td>
<td>0.23(0.03)</td>
<td>1.3(0.1)</td>
<td>2.15(0.05)</td>
</tr>
<tr>
<td>Co⁺ + [O + CH₄] + H + H</td>
<td>0.25(0.01)</td>
<td>1.5(0.1)</td>
<td>1.53(0.08)</td>
</tr>
</tbody>
</table>

*Uncertainties of one standard deviation are in parentheses.

Figure 2. Cross sections for reactions of CoO⁺ with D₂ as a function of kinetic energy in the center-of-mass frame (lower axis) and laboratory frame (upper axis).

with two contributions to eq 4 as given in Table 2. The high energy part begins at an energy consistent with either reaction 8b or 8c. Analysis of the cross section below 3 eV yields E0 = 0.60 ± 0.15 eV, within experimental error of the threshold measured for reaction 7, 0.75 ± 0.04 eV. It was verified that both of these threshold measurements did not depend on the pressure of the D₂ reactant within the cited experimental error.

Our results for this system differ from those of Schröder et al., who found that only reaction 8a was observed with a thermal rate constant of 1.2 × 10⁻¹¹ cm³/s. Below 0.4 eV, our cross sections for this reaction and for reaction 7 have reached the noise level and are both about (3 ± 5) × 10⁻¹³ cm²/s, respectively. If our data are converted to rate constants, the values are about 0.9 ± 1.5 × 10⁻¹³ cm³/s for both reactions. Both the cross sections and rate constants are probably best viewed as upper limits. The reasons behind the discrepancy between our rate constant and that of Schröder et al. are unclear.

Co⁺ + CH₃OD. Transitionally excited cobalt ions react with methanol deuterated at the hydroxy position to yield seven ionic products, formed in reactions 10-16.

CO⁺ + CH₃OD → CoOD⁺ + CH₃ - 0.84 ± 0.09 eV (10)
→ CoCH₃⁺ + OD - 1.84 ± 0.04 eV (11)
→ CH₂OD⁺ + CoH - 1.92 ± 0.05 eV (12)
→ CoH⁺ + CH₂OD - 2.12 ± 0.06 eV (13)
→ CoOCH₃⁺ + CoH - 2.52 ± 0.07 eV (14)
→ CoOCH₃⁺ + D (15)
→ CoCH₂⁺ + HOD - 0.22 ± 0.06 eV (16)

These results are shown in Figure 3. Reactions 10 and 11, which correspond to activation of the C–O bond, dominate the product spectrum at low energies. Competition between the CoOD⁺ and CoCH₃⁺ products is suggested by the observation that the former cross section reaches a peak at the threshold for the latter. These products both decline rapidly above ~4 eV, which corresponds to D0(CH₃-OD) = 3.940 ± 0.005 eV, indicating that they decompose to Co⁺ + CH₃ + OD. Activation of the C–H bond leads to reactions 12 and 13, where the products differ only in the location of the charge. These reactions are the most likely processes at high energies, in part because of angular momentum considerations. Activation of the single O–D bond is energetically and statistically less favorable than activation of the three available C–H bonds. This is reflected in the small size of the CoD⁺ and CoOCH₃⁺ products. Note that the CoOCH₃⁺ cross section peaks at the threshold for CoD⁺ formation, indicating competition between these products. Also, the complex rearrangement of the reactants to eliminate water, reaction 16, is relatively unlikely.

Analyses of these various cross sections yield the optimum parameters given in Table 2. The thresholds for reactions 10–12 are in good agreement with those calculated from literature thermochemistry. The cross section for CoH⁺ is somewhat scattered because this product has a mass close to that of the
much more intense reactant. This makes analysis of the data difficult, although this cross section is easily reproduced if the thermodynamic threshold is used in eq 4. Analysis of the cross section for reaction 14 yields an $E_0$ value that is slightly larger than the thermodynamic value, but well below that for production of CoD$^+$ + CH$_3$O + H, 3.43 ± 0.06 eV. The measured threshold is probably elevated because of competition with the other much more likely reaction channels. The small size of the CoOCH$_3^+$ cross section makes definitive analysis difficult, although an estimate of the threshold is 1.5 ± 0.3 eV. Analysis of the CoCH$_2^+$ cross section yields $E_0 = 0.90 ± 0.08$ eV, considerably above the thermodynamic threshold of 0.22 ± 0.06 eV. This may be due to competition with the other more likely channels, but the complexity of this rearrangement means that the possibility of a reaction barrier needs to be considered, as discussed further below.

As in the Co$^+$ + D$_2$O system, CoO$^+$ was not observed in the reaction of Co$^+$ with CH$_3$OD even though formation of CoO$^+$ + CH$_3$D has the second lowest overall reaction endoergicity, 0.60 ± 0.05 eV (ignoring the effects of deuterium substitution). A careful search for this product indicates that its cross section is less than 0.02 Å$^2$.

CoO$^+$ + CH$_4$. Translationally excited cobalt oxide ions react with methane to form five ionic products, corresponding to processes 17-21, as shown in Figure 3.

\[
\text{CoO}^+ + \text{CH}_4 \rightarrow \text{CoOH}^+ + \text{CH}_3 - 0.24 \pm 0.10 \text{ eV (17)}
\]

\[
\rightarrow \text{Co}^+ + \text{CH}_3\text{OH} + 0.60 \pm 0.05 \text{ eV (18a)}
\]

\[
\rightarrow \text{Co}^+ + \text{O} + \text{CH}_4 - 3.25 \pm 0.05 \text{ eV (18b)}
\]

\[
\rightarrow \text{Co}^+ + \text{OH} + \text{CH}_3 - 3.34 \pm 0.05 \text{ eV (18c)}
\]

\[
\rightarrow \text{CoH}^+ + \text{CH}_2\text{O} + \text{H} - 2.79 \pm 0.08 \text{ eV (19)}
\]

\[
\rightarrow \text{CoOCH}_3^+ + \text{H} \quad (20)
\]

\[
\rightarrow \text{CoOCH}_2^+ + 2 \text{ H} \quad (21)
\]

It can be seen that the cross sections for reactions 17 and 18 behave similarly to those for the analogous reactions 7 and 8 in the CoO$^+$ + D$_2$ reaction system. Also, the products observed in this system are similar to those seen in the Co$^+$ + CH$_3$OD system, with the notable absence of CoCH$_3^+$, CH$_2$O$^+$ (corresponding to the CH$_2$OD$^+$ product), and CoCH$_2^+$ (even though formation of CoCH$_3^+$ + H$_2$O is exothermic by 0.37 ± 0.08 eV). Searches for these three products were conducted and our failure to observe them indicates they have cross sections less than 0.02 Å$^2$, although efficient detection of the CoCH$_3^+$ product is more problematic because it is only one mass unit away from the much more intense reactant ion.

As in the CoO$^+$ + D$_2$ system, the exothermic oxidation reaction 18a, does not occur until overcoming an activation barrier of 0.5-1.0 eV, nearly the same energy required to form CoOH$^+$, the dominant product at low energies. It was verified that these reaction cross sections are not dependent on the pressure of the CH$_4$ reactant within our experimental error. Reactions 18b and 18c account for the increased production of Co$^+$ observed above ~3 eV. Competition between the Co$^+$ and CoOH$^+$ channels is suggested by the smooth variation in the total cross section with energy. Analysis of the cross section for CoOH$^+$ with eq 4, Table 2, yields $E_0 = 0.56 ± 0.08$ eV, about 0.3 eV larger than the thermodynamic threshold of 0.24 ± 0.10 eV. The data cannot be reproduced well if the thermodynamic threshold is used in eq 4. Analysis of the Co$^+$ cross section is difficult because this cross section rises very slowly and has both low and high energy components. The low energy portion of the data can be reproduced nicely with $E_0 = 0.56 ± 0.08$ eV, the same as for the CoOH$^+$ channel. The high energy portion of the Co$^+$ cross section can be reproduced by adding a cross section beginning at 3.29 ± 0.07 eV, consistent with reactions 18b and 18c.

Formation of both CoOCH$_3^+$ + H and CoOH$^+$ + CH$_3$ involves activation of the C-H bond of methane followed by loss of one of the radicals thus formed. Production of CoOCH$_3^+$ appears to be suppressed because it has a threshold 1.6 eV higher than that for CoOH$^+$, Table 2. Also angular momentum constraints inhibit this channel relative to the CoOH$^+$ channel. Formation of CoOCH$_3^+$ appears to proceed by hydrogen atom loss from the CoOCH$_2^+$ based on its high threshold energy and its energy dependence, but the cross section is too small to analyze definitively. Analysis of the CoH$^+$ cross section, Table 2, yields...
This indicates that their cross sections are less than 0.01 Å². This is due to the strong competition from the CID reaction which suppresses all but the major reactions observed in the bimolecular Co⁺ + CH₃OD reaction system.

Analysis of the cross section for reaction 22 yields the optimum parameters given in Table 2. Analysis of the CoOD⁺ cross section is difficult, because this cross section appears to have both a low-energy component and a high-energy component, obvious above about 12 eV. If the calculated, thermodynamic threshold of 2.34 ± 0.09 eV (the sum of the thresholds for reactions 10 and 22) is used in eq 4, the low-energy portion of the cross section can be reproduced. The high-energy portion may be due to a distinct pathway for formation of CoOD⁺ or to another isomer, D–Co⁺–O, which would lie about 2.3 eV higher than CoOCH₃⁺ assuming that D₀(OCO⁻–D) = D₀(CO⁺–D). Analysis of reaction 24 was not performed because the cross section is small and rises slowly from its onset.

Thermochemical Results. (a) CoOH⁺. As shown in Figures 1–5, CoOD⁺ or COOH⁺ is observed in all five of the reaction systems studied here. In the following discussion, we assume that the Co⁺–OH and Co⁺–OD bond energies are identical, a reasonable assumption, as discussed elsewhere. Thresholds measured for reactions 6, 7, 10, and 17 lead to Co⁺–OH bond energies of 3.10 ± 0.12, 2.60 ± 0.07, 3.13 ± 0.04, and 2.78 ± 0.10 eV. The two larger values agree with the literature: 3.12 ± 0.13 eV obtained from a CID study by Magnera, David, and Michel, and 3.08 ± 0.13 eV obtained by photodissociation of COOH⁺ by Cassady and Freiser. Therefore, we accept the weighted average of the measurements from reactions 6 and 10, 3.13 ± 0.04 eV, as our best determination of the CoOH⁺ bond energy at 0 K and conclude that reactions 7 and 17 exhibit thresholds that are higher than their thermodynamic endothermicities (thus leading to calculated Co⁺–OH bond energies that are lower than the other values). This conclusion is consistent with the observation that the associated reactions 8a and 8b also exhibit thresholds, even though both reactions are exothermic.

We note that the Co⁺–OH bond energy is considerably larger than D₀(Co⁺–CH₃) and D₀(Co⁺–H), Table 1, even though OH, CH₃, and H can form only one covalent bond with another species. The enhancement in the metal ion–hydroxide bond energy is due to donation of the two lone pairs of electrons on oxygen into half-occupied 3d orbitals on Co⁺, as discussed in more detail elsewhere.

(b) CoCH₃⁺. The measured threshold for reaction 11, 1.84 ± 0.08 eV, coupled with D₀(CH₃OD) = 3.940 ± 0.005 eV yields a bond energy of D₀(COCH₃⁺) = 2.10 ± 0.08 eV. This value is in good agreement with the value of 2.10 ± 0.04 eV, obtained from previous studies in our laboratory.

(c) CoD⁺ and CoH. The threshold measured for reaction 5, 3.16 ± 0.05 eV, coupled with D₀(DO–D) = 5.212 ± 0.001 eV, Table 1, leads to D₀(Co⁺–D) = 2.05 ± 0.05 eV, in good agreement with our previous value, 2.01 ± 0.06 eV. In contrast, the measured thresholds for reactions 9 and 14 cannot be used to derive accurate values for D(Co⁺–D) because of the strong competition from other major reaction channels.

The measured threshold for reaction 12, 1.89 ± 0.06 eV, Table 2, can be used to derive the bond energy of neutral cobalt hydride by using eq 25,

\[ D₀(CO–H) = D₀(DOCH₂⁺H⁻) + E₀ – IE(CO) + EA(H) \]

(25)

where D₀(DOCH₂⁺H⁻) is assumed to equal D₀(HOCO⁺⁻H⁻) = 10.89 ± 0.01 eV. IE(CO) is the ionization energy of Co, 7.864 ± 0.001 eV, and EA(H) is the electron affinity of H, 0.754 eV.²


This gives a bond energy of \( D_0(\text{Co}-\text{H}) = 1.89 \pm 0.06 \) eV, in good agreement with previous results from our laboratory, 1.86 \pm 0.05 eV.\(^{38}\)

(d) \( \text{CoOCH}_3 \). The estimated threshold for reaction 15, 1.5 \( \pm 0.3 \) eV, leads to \( D_0(\text{Co}^\ast-\text{OCH}_3) = 3.0 \pm 0.3 \) eV, consistent with a lower limit of 1.8 eV that can be derived from work of Freiser and co-workers.\(^{33}\) Our value seems reasonable when compared with \( D_0(\text{Co}^\ast-\text{OH}) = 3.13 \pm 0.04 \) eV, Table 1. Also, this threshold indicates that \( D_0(\text{Co}^\ast-\text{CH}_3) = 3.6 \pm 0.3 \) eV, comparable to the \( \text{C}-\text{O} \) bond energy in methanol, \( D_0(\text{H}_2\text{C}-\text{OH}) = 3.93 \) eV. In contrast, the measured threshold for reaction 20, 2.15 \( \pm 0.05 \) eV, leads to much smaller values, \( D_0(\text{Co}^\ast-\text{CH}_3) = 1.72 \pm 0.08 \) eV and \( D_0(\text{OCO}^\ast-\text{CH}_3) = 2.33 \pm 0.05 \) eV. The latter bond energy is comparable to \( D_0(\text{Co}^\ast-\text{CH}_3) = 2.10 \pm 0.04 \) eV, suggesting that reaction 20 actually forms a different isomer, \( \text{OCO}^\ast-\text{CH}_3 \), rather than the cobalt–methoxy ion. Because it is possible that the relatively minor reactions 15 and 20 are suppressed by the other major reaction channels, these bond energies are most conservatively viewed as lower limits.

(e) \( \text{Co}^\ast(\text{CH}_3\text{OH}) \). The bond energy of \( \text{Co}^\ast-\text{CH}_3\text{OD} \) is directly measured from the threshold of reaction 22, Table 2. The effects of deuterium substitution on this bond energy should be small, and therefore this threshold, 1.53 \( \pm 0.08 \) eV, should also be a measurement of \( D_0(\text{Co}^\ast-\text{CH}_3\text{OH}) \). It is interesting to note that this bond energy is slightly smaller than \( D_0(\text{Co}^\ast-\text{H}_2\text{O}) = 1.67 \pm 0.06 \) eV,\(^{39}\) although the values are at the edge of the combined experimental errors. It is not clear whether this small difference is statistically significant, but it might be rationalized because the dipole moment of methanol is smaller than that of water.

**Discussion**

**Reaction Mechanisms and Potential Energy Surfaces.** (a) \( \text{Co}^\ast + \text{D}_2\text{O} \) and \( \text{CoO}^\ast + \text{D}_2 \). There are two reasonable mechanisms for the interaction of \( \text{Co}^\ast \) with \( \text{D}_2\text{O} \): \( \text{Co}^\ast \) insertion into a \( \text{D}_2 \) bond to form a \( \text{D} \)-\( \text{Co}^\ast \)-\( \text{OD} \) intermediate, I, or direct abstraction of the \( \text{D} \) atom or the \( \text{OD} \) group by \( \text{Co}^\ast \). Oxidative addition of a covalent bond to first-row transition metal ion centers is believed to be most facile when the metal has an empty 4s orbital to accept the pair of electrons in the covalent bond, and when it has a pair of 3d electrons of proper symmetry to donate into the antibonding orbital for the bond.\(^{40}\) The \( ^1\text{F}(3\text{d}) \) ground state\(^{41}\) of \( \text{Co}^\ast \) has a suitable electron configuration for this oxidative addition reaction. Moreover, if the \( \text{CoD} \) and \( \text{CoOD} \) bonds in the insertion intermediate are covalent, then there will be six nonbonding electrons in four orbitals closely spaced in energy such that this species should have a triplet spin ground state. Thus, formation of I from the ground state \( \text{Co}^\ast(3\text{F}) + \text{D}_2\text{O}(\text{A}_1) \) reactants should conserve spin.

Clearly, intermediate I can decompose to form \( \text{CoD}_2 \) + \( \text{OD} \), reaction 5, and \( \text{CoOD}^\ast + \text{D} \), reaction 6, by simple bond fissions. Both reactions conserve spin as both neutral products have doublet spin and both ionic products have quartet spin.\(^{42}\) The strong experimental observation between these two reactions is consistent with a common intermediate, which is depleted by both reaction channels. A direct abstraction mechanism cannot easily account for this competition, although direct pathways could contribute to the observed reactions, especially at higher kinetic energies.

Figure 6a shows a qualitative potential energy surface for the \( \text{Co}^\ast + \text{D}_2\text{O} \) reaction. The initial interaction is attractive because of the long-range ion–dipole potential. Thus, there is a well corresponding to the \( \text{Co}^\ast \)-\( \text{OD} \) complex, which has a \( ^3\text{B}_2 \) ground state according to theoretical calculations.\(^{44}\) The energy of this complex is taken as the \( \text{Co}^\ast-\text{OH}_2 \) bond energy, 1.67 \( \pm 0.06 \) eV, Table 1.\(^{28,39,44}\) The energy of intermediate I is estimated to be 0.07 \( \pm 0.07 \) eV, based on the bond additivity assumption that \( D_0(\text{DOC}^\ast-\text{OD}) = D_0(\text{Co}^\ast-\text{D}) \). (Although this assumption may not be quantitatively accurate, it is the only reasonable means of estimating the energy of I.) The transition state between the \( \text{Co}^\ast-\text{OD}_2 \) complex and I is likely to correspond to a barrier, as discussed further below, but the height of this barrier cannot be quantitatively assessed from our experiments other than to note that it cannot be higher than the energy of the \( \text{CoOD}^\ast + \text{D} \) products.}

\(^{38}\) Fisher, E. R.; Armentrout, P. B. J. Phys. Chem. 1990, 94, 1674. The value cited here has been reevaluated to 0 K, as discussed in ref 9.

\(^{39}\) Pettersson, L. G. M.; Bauschlicher, C. W.; Langhoff, S. R. J. Chem. Phys. 1987, 87, 4811. CoCH\(_3\)H has a \( ^3\text{E} \) ground state (Bauschlicher, C. W.; Langhoff, S. R.; Partridge, H.; Barnes, L. A. J. Chem. Phys. 1989, 91, 2399). If the \( \text{Co}^\ast-\text{OD} \) bond has covalent character, which seems certain, then it also should have a quartet spin ground state. CH\(_3\)- has a Sanz state (Jacox, M. E. J. Phys. Chem. Ref. Data, 1984, 13, 945). OD\(_2\) and D\(_2\) have \( ^3\text{II} \) and \( ^3\text{E} \) ground states, respectively (Huber, K. P.; Herzberg, G. Molecular Spectra and Molecular Structure, IV, Constants of Diatomic Molecules, Van Nostrand Reinhold: New York, 1979).
thermodynamic one. No barriers in excess of the endothermicity to formation of CoOD\(^+\) + D or CoD\(^+\) + OD are found experimentally, consistent with simple bond fission reactions from I. The former product channel is favored thermodynamically, but the latter channel is favored kinetically due to angular momentum considerations, as noted above.

Although formation of CoO\(^+\) + D\(_2\) is the most favorable channel thermodynamically, it is not observed for two reasons. First, there is a barrier to this channel in excess of the endothermicity, as exhibited for the reverse reaction 8a, exothermic by 1.86 ± 0.05 eV. Second, this barrier corresponds to a tight transition state and hence this channel is kinetically hindered, as suggested by the failure to observe CoO\(^+\) + D\(_2\) products even when sufficient energy to overcome the barrier is supplied to Co\(^+\) + D\(_2\)O reactants. We attribute this tight transition state to the four-centered transition state II, Figure 6a, in which the D\(_2\) adds across the CoO\(^+\) bond. This is based on our previous detailed discussion of the reactions of D\(_2\) with ScO\(^+\), TiO\(^+\), and VO\(^+\), in which three possible mechanisms were considered: addition at the metal end of MO\(^+\), addition at the O end, or addition across the MO\(^+\) bond. Molecular orbital considerations suggested that the latter should be the most facile pathway.\(^7\) For similar reasons, we discount the possibility that a direct abstraction reaction of CoO\(^+\) + D\(_2\) to form CoOD\(^+\) + D is a low energy (barrierless) pathway because this mechanism would involve the interaction of D\(_2\) with the oxygen end of CoO\(^+\) (where there are no empty or half-filled orbitals).

This potential energy surface also allows our observations regarding the reverse reaction of CoO\(^+\) + D\(_2\) to be easily understood. The initial long-range ion-induced dipole interaction between CoO\(^+\) and D\(_2\) may lead to the formation of CoO\(^+\)-D\(_2\)\(^-\), and we estimate the strength of this interaction as comparable to that measured by Kemper et al. for Co\(^+\)-H\(_2\), 0.79 ± 0.04 eV.\(^45\) No further reaction can take place until the barrier corresponding to II is overcome. Thus, formation of both Co\(^+\)-D\(_2\)O and CoOD\(^+\) + D is observed to have a common threshold, because these processes have thermodynamic thresholds below the barrier height. We take the barrier height to be 0.75 ± 0.04 eV above the CoO\(^+\) + D\(_2\) asymptotic energy, the threshold measured for reaction 7 and consistent with but more precise than that measured for reaction 8a.

Initially, we thought that the observation that CoOD\(^+\) + D formation is more favorable than Co\(^+\) + D\(_2\)O formation might suggest that there is a sizable barrier between CoO\(^+\)-OD\(_2\) and intermediate I, otherwise the transiently formed I should efficiently eliminate water because this channel is thermodynamically much more favorable. The presence of a barrier would mean that this channel is kinetically hindered and therefore does not compete effectively with the simple bond fission leading to CoOD\(^+\) + D. Phase space theory (PST) calculations for this system, see below, find that this nonintuitive branching ratio is partially explained by statistical considerations, namely that the density of ro-vibrational states for CoOD\(^+\) increases more rapidly than that for D\(_2\)O. Including a barrier between CoO\(^+\)-OD\(_2\) and intermediate I seems intuitively reasonable and can help the PST calculations reproduce the experimental behavior, but the calculations indicate that such a barrier need not be large in order to explain the data.

In contrast to the reaction of Co\(^+\) + D\(_2\)O, formation of CoO\(^+\) + OD from CoO\(^+\) + D\(_2\) is not dominant at high energies, because angular momentum considerations do not play as significant a role, as noted above. This is a combination of the change in reduced mass of the reactants and the differing energetics. As in the Co\(^+\) + D\(_2\)O system, direct abstraction reactions may also contribute to the reactivity observed for CoO\(^+\) + D\(_2\), but such a mechanism cannot easily explain the competition between the formation of CoOD\(^+\) + D and CoO\(^+\) + D\(_2\)O, nor the observation of CoO\(^+\) + OD.

---


(b) Co\(^+\) + CH\(_3\)OD and CoO\(^+\) + CH\(_4\) On the basis of the similarities in the reaction cross sections, we propose that the reaction mechanism and potential energy surfaces for the activation of the C-O bond of methanol by Co\(^+\) and for the reaction of CoO\(^+\) with CH\(_4\) are quite similar to those for the Co\(^+\) + D\(_2\)O and CoO\(^+\) + D\(_2\) reaction systems. This is shown in Figure 6b, where the energies of the various intermediates are estimated as above. The primary difference between the two systems is the energetics of the Co\(^+\) + ROD species and the Co\(^+\)-ROD adduct (where R = D or CH\(_3\)) relative to all other channels and intermediates.

Differences in the product distributions between the forward and reverse reactions are now easily understood. For the CoO\(^+\) + CH\(_4\) system, addition of a C-H bond across the CoO\(^+\) bond can lead to two intermediates, CH\(_3\)-CoO\(^-\)-OH (III) and H-CoO\(^-\)-CH\(_2\)O (IV). Because CoO\(^+\)H\(^+\) is the major ionic product observed in this reaction, Figure 4, the formation of the former intermediate is clearly favored. This can be rationalized on the basis that an O-H bond is stronger than a C-O bond, but the Co\(^+\)-H and Co\(^+\)-CH\(_2\)O bond strengths are similar, Table 1. Indeed, our analysis of the CoOCH\(_3\)\(^+\) product formed in reaction 20 can be interpreted to indicate that intermediate IV may not be formed at all. As noted above, the threshold measured for reaction 20 is more consistent with formation of OCO\(^+\)-CH\(_3\) which can be formed directly from III by H atom loss, than it is with formation of a cobalt methoxy ion, Co\(^+\)-OCH\(_3\) which could be formed easily from IV. The CoH\(^+\) product observed, Figure 4, may suggest that intermediate IV is formed, but its measured threshold is more consistent with CH\(_2\)O + H neutral products than with CH\(_3\)O as would be expected for a simple bond fission from IV. The mechanism for CoH\(^+\) + CH\(_3\)O + H formation from III is necessarily complex, but a rearrangement of the OCO\(^+\)-CH\(_3\) product to the more stable Co\(^+\)-OCH\(_3\) isomer is a plausible first step.

In addition to activation of the H\(_3\)C-OD bond, the Co\(^+\) ion can also activate the CH\(_3\)O-D or H-CH\(_2\)OD bond of the CH\(_3\)OD molecule to form the D-CoO\(^-\)-CH\(_3\) (IV) or H-CoO\(^-\)-CH\(_2\)OD (V) intermediates. V cannot be formed directly from the CoO\(^+\) + CH\(_4\) reactants and hence products resulting from this intermediate, CoH\(^+\) + CH\(_2\)OD and CH\(_2\)OD\(^+\) + CoH, are absent in Figure 4. The presence of I in the reaction of Co\(^+\) + CH\(_3\)OD is suggested by the observation of CoD\(^+\) + OCH\(_3\) (where the measured threshold, 2.80 ± 0.12 eV, is closer to the thermodynamic threshold for OCH\(_3\) as the neutral product, 2.52 ± 0.07 eV, than that for CH\(_2\)OH as neutral product, 2.15 ± 0.06 eV) and CoOCH\(_3\)\(^+\) + D (where the threshold is consistent with the cobalt methoxy ion isomer, as discussed above).

Finally, the reaction of Co\(^+\) with CH\(_3\)OD forms CoOCH\(_3\)\(^+\) + HOD, which can be formed by eliminating HOD from the CH\(_3\)-Co\(^+\)O or H-CoO\(^+\)-CH\(_2\)OD intermediates. Presumably, this must proceed through a tight transition state, thereby explaining why the reaction is inefficient and has a measured threshold exceeding its thermodynamic value. We assign the measured threshold of 0.90 ± 0.08 eV to the height of this barrier relative to the Co\(^+\) + CH\(_3\)OD reactants (0.68 ± 0.10 eV relative to products). We note that this barrier is comparable to the barrier leading to CoO\(^+\) + CH\(_3\)D, 1.16 ± 0.06 eV relative to reactants (0.75 ± 0.04 eV relative to products). This latter process is not observed, presumably because of competition with formation of CoOD\(^+\) + CH\(_3\), which has a threshold lower than the barrier height. The simplest explanation for why the CoCH\(_3\)+ + HDO products are observed is that this reaction proceeds by intermediate IV, where the competing bond fission processes leading to CoH\(^+\) + CH\(_3\)OD and CH\(_2\)OD\(^+\) + COH do not begin until energies higher than the barrier. Indeed, the CoCH\(_3\)+ cross section does level off near the thresholds for these channels, Figure 3.

Comparison of D\(_2\) + Co\(^+\) Reactivity with That of D\(_2\) + Co\(^+\), ScO\(^+\), TiO\(^+\), and VO\(^+\). In our study of the reactions of ScO\(^+\),
Conversion of CH₄ to CH₃OH

TiO⁺, and VO⁺ with D₂, insight into the details of the reactivity of MO⁺ was gained by comparing these systems to the results for reaction of the bare metal ions with D₂, reaction 26.

M⁺ + D₂ → MD⁺ + D

(26)

The analogous process to reaction 26 for the metal oxides is formation of MOD⁺ + D. In the present system, the maximum magnitude of σ(CoOd⁺) formed from the reaction of CoO⁺ + D₂ is ~2.0 Å². Figure 2, similar to the ~1.8 Å² magnitude measured for the reaction of Co⁺(F)⁺. This similarity in magnitudes is found despite the fact that reaction 26 is endothermic by 2.55 ± 0.06 eV for Co⁺ while reaction 7 is endothermic by only 0.22 ± 0.06 eV (based on the thermochemistry measured here). The barrier shifts the observed threshold for reaction 7 to 0.75 ± 0.04 eV, but thermodynamically, reaction 7 is still much more favorable than reaction 26. This suggests that there is some additional kinetic constraint in the efficiency of reaction 7.

It is also interesting to compare the reactivity of CoO⁺ + D₂ with that of ScO⁺, TiO⁺, and VO⁺ + D₂. In the latter three systems, formation of MOD⁺ + D is endothermic by 1.6–2.2 eV, with no barriers in excess of the reaction endotherm. Note that these endothermicities are sufficiently large that they would exceed the height of a barrier similar to that measured here for the M = Co system. The same is true for the endothermicities for reaction 26 + D₂ in these three early metal systems. Thus, the failure to observe a barrier in these three systems is still consistent with the observation of a barrier in the cobalt system.

Electronic States of COO⁺ and the Activation Barrier. The conversions of CH₄ to CH₃OH and of D₂ to D₂O by COO⁺ are exothermic reactions, and we previously anticipated that these reactions might be efficient because of this. Instead, the present study shows that they are inefficient due to the restrictions of reaction 7. For COO⁺, the ground state is 3Σ⁺(8s²3p²9s²16δ¹⁴σ²), 1Σ⁺(8s²3p²9s²16δ¹⁴σ²), 3Δ(8s²3p²9s²16δ¹⁴σ²), 2Π(8s²3p²9s²16δ¹⁴σ²), and 3Σ⁻(8s²3p²9s²16δ¹⁴σ²). Based on the comparison with FeO⁺, it seems likely that either 3Σ⁻ or 3Δ is the ground state of CoO⁺ with 3Σ⁻ being low-lying excited states and the 3Σ⁻ state lying somewhat higher in energy. After this paper was submitted for publication, we received results of ab initio calculations on CoO⁺ performed by Fiedler et al. They obtain a 3Δ ground state and excited states of 3Σ⁻ at 1.0 eV, 2Π at 1.2 eV, and 3Δ at 1.4 eV, confirming the qualitative considerations given above.

In our previous paper, analysis of the molecular orbital (MO) interactions between MO⁺ and H₂ or CH₄ suggested that the oxidation reactions should be efficient when the metal oxide has an empty mo that can accept electron density from the bond to be broken and an occupied MO having the correct symmetry to donate electron density into the antibonding mo of the bond to be broken. Likely acceptor and donor MOs were identified as 9e and either 3α or 4α, respectively. ScO⁺, TiO⁺, and VO⁺ all have ground-state electron configurations that meet these criteria, thereby explaining why they react efficiently with D₂ despite high reaction endothermicities.

In our previous analysis of the likely reactivity of CoO⁺, we assumed that the ground state of CoO⁺ was 3Σ⁺ because this state correlates to ground state Co⁺(F, 3d⁰). In contrast to the conclusions reached above based on the calculations of Fiedler et al., the 3Σ⁻ state has an empty 9e and occupied 3α and 4α molecular orbitals. Thus reaction 3 was predicted to be efficient because it conserves spin and CoO⁺(3Σ⁻) has a favorable electron configuration for reaction. If the ground state of CoO⁺ is 3Δ or 3Σ⁺, however, inefficient reaction with D₂ and CH₄ is easily rationalized. These CoO⁺ states have occupied 9e orbitals, leading to more repulsive interactions with D₂ and CH₄. Likewise, the high-lying 3Π and 3Π states of CoO⁺ may have repulsive interactions with these molecules because they have an occupied 9e orbital as well. These considerations also explain the relative inefficiency of reaction 7 compared to that of reaction 26, as noted above. CoO⁺ has an occupied 9e mo while Co⁺ has an empty 4s acceptor orbital, and the additional kinetic constraint to reaction 7 is that this reaction no longer conserves spin while reaction 26 does.

If this MO picture is qualitatively correct, we speculate that the potential energy surfaces for interaction of CH₄ and D₂ by analogy with CoO⁺ in these various states may be as shown in Figure 7. The excited CoO⁺(3Σ⁻) state is presumed to bind CH₄ (or D₂) more strongly and with a shorter bond distance than the other states where the 9e mo is occupied. This surface then diabatically leads to formation of the ground-state R-CoO⁺–OH intermediate, and from there to the other products observed. Crossings between the quintet and triplet surfaces can interact by spin–orbit coupling. The barrier height measured in this study can be associated with the barrier along either the low-spin surface, Figure 7a, or the high-spin surface, Figure 7b. In the former case, the observed reactivity occurs by transferring from the high-spin to the low-spin surface, thereby explaining the inefficient reactivity as due to the spin-forbidden nature of the reaction. In the latter case, the observed reactivity occurs in a spin-allowed fashion along the high-spin surface, thereby explaining the inefficient reactivity as due to reaction along an unfavorable excited state surface. Clearly, these qualitative potential energy surfaces can be improved as more advanced information regarding the states of CoO⁺ becomes available.

The surfaces shown in Figure 7b are consistent with those

References

CH$_3$-H is 0.08 eV weaker than that of D-D and the Co$^+$-CH$_3$ bond is 0.09 eV stronger than the Co$^+$-D bond, Table 1. The depths of the potential wells of CoO$^+$.RH complexes are estimated as equivalent to $D_0$(Co$^+$-CH$_3$) = 0.99 eV for RH = CH$_4$ and $D_0$(Co$^+$-H$_2$) = 0.79 eV for RH = D$_2$. Apparently, these thermodynamic factors allow the barrier for activation of methane to move below that for activation of deuterium, such that activation of C-H bonds is facilitated by interaction with metal oxide ions compared to that with bare metals.

**Consideration of Kinetic and Competitive Shifts.** Phase Space Modeling. Although the picture of these reaction systems developed above is self-consistent, it is important to consider the possibility that the thresholds for reactions 7 and 8a might be affected by kinetic shifts, i.e., that these reactions take a longer time than that available in our experimental apparatus and hence the first observation of a reaction is delayed until an energetic where the kinetics are sufficiently fast that we observe them. We first note that a kinetic shift, if it exists, can only be influencing our measurement of the height of the barrier, not whether there is a barrier along the potential energy surfaces for these reactions. This is based on our observation of common thresholds for reactions 7 and 8a and reactions 17 and 18a, pairs of reactions that have very different energetics and almost certainly have very different kinetics.

In considering the kinetic question further, it should be remembered that kinetic shifts are usually discussed in terms of unimolecular reactions where kinetic shifts occur because an energized ion does not dissociate on the experimental time scale. Thus, the parent ion is observed rather than the product ions. In the bimolecular reactions studied here, kinetic shifts would occur when the energized molecule formed from the reactants (i.e., CoO$^+$.D$_2$ or CoO$^+$-CH$_4$, the adducts of the reactants) is observed rather than the product ions. In our apparatus, the flight time of the ions from the collision chamber to the detector quadrupole is about $10^{-4}$ s. It seems highly unlikely that the CoO$^+$.D$_2$ or CoO$^+$-CH$_4$ species have lifetimes exceeding this, and indeed no adduct species were observed in our studies within a limit of better than $10^{-2}$ Å. If kinetic shifts were to explain the discrepancy between our observations and those of Schröder et al., who observed reaction 8a with the rate constant of $1.2 \times 10^{-12}$ cm$^3$ s$^{-1}$, then we should have seen the CoO$^+$.D$_2$ adduct with a cross section of $3 \times 10^{-12}$ Å$^2$.

Another possible way that the thresholds measured here could be shifted from the true barrier height is if there is severe competition between the channels of interest and some other channel. In the CoO$^+$.D$_2$ reaction system, these are the CoOD$^+$ + D and Co$^+$ + D$_2$O product channels, whereas the only possible competitive channel is dissociation of the CoO$^+$.D$_2$ adduct to reform the CoO$^+$ + D$_2$ reactant ions (a process that we cannot observe directly). Under the conditions used in these experiments, we can observe reaction efficiencies as small as $10^{-4}$, such that this competition must favor reforming the reactants by a factor larger than 10$^4$, otherwise we would observe the CoOD$^+$ + D and Co$^+$ + D$_2$O products. Similar considerations hold for the analogous methane system.

To further test whether this type of competition could influence our measurement of the reaction thresholds, we have carried out a phase space theory (PST) calculation for the reaction of CoO$^+$ with D$_2$. We have previously detailed our use of PST for this type of calculation, and use codes that are adapted from those of Bowers, Chesnavich, and others. In a PST calculation, reactions are assumed to proceed through a strongly coupled

---

(55) Haynes, C. L.; Armentrout, P. B., work in progress.
(57) Programs are now available from the Quantum Chemistry Program Exchange, Indiana University, program No. 557. Contributors to the original and revised programs include Bowers, M. T.; Chesnavich, W. J.; Jarrold, M. F.; Bass, L.; Grice, M. E.; Song, K.; Webb, D. A.
Table 3. Molecular Constants (in cm⁻¹) Used in Phase Space Calculations

<table>
<thead>
<tr>
<th>species</th>
<th>ω₀ (ω₀X₀)</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co⁺O⁺</td>
<td>850 (6)³</td>
<td>0.5⁵</td>
</tr>
<tr>
<td>OD⁻</td>
<td>2720 (44.1)</td>
<td>10.02</td>
</tr>
<tr>
<td>D⁺O⁻</td>
<td>3116 (61.8)</td>
<td>30.44</td>
</tr>
<tr>
<td>D₂O⁺</td>
<td>2784 (56.2), 1206 (13.8), 2889 (50.4)</td>
<td>8.18⁸</td>
</tr>
<tr>
<td>CoOD⁺</td>
<td>2400 (42), 700 (6), 300 (4)</td>
<td>1.1, 1.3³</td>
</tr>
<tr>
<td>Co⁺D⁻</td>
<td>1350 (35)</td>
<td>3.7</td>
</tr>
<tr>
<td>T.S.¹</td>
<td>530, 700, 740, 990, 1140</td>
<td>0.62²</td>
</tr>
</tbody>
</table>


A rotational constant of 1.3 cm⁻¹ was estimated by using structural information for a high-spin H-Fe⁺-OH intermediate (except where H is eliminated) calculated in ref 51. A value of 1.1 cm⁻¹ is found to match the experimental data better, see text. ⁹ Vibrational constant is estimated by using a Morse potential to scale the frequency of CoH⁺ from: Fiedler et al. ⁵¹ for the analogous four-centered transition state and both sets of parameters were tried in our calculations. ¹⁰ Transition state in the entrance channel. Vibrational frequencies are estimated from values for the corresponding CoOCH₂⁺ species as calculated in ref 51. The rotational constant is estimated from the structural information of the analogous FeOH⁺ species as calculated in ref 51.

Table 4. Parameters Used in Phase Space Calculations

<table>
<thead>
<tr>
<th>reaction channel</th>
<th>reduced mass (amu)</th>
<th>polarizability of neutral (Å³)</th>
<th>symmetry</th>
<th>no.* surfaces²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO⁺(2Σg) + D₂(2Σg)</td>
<td>3.82</td>
<td>0.775⁶</td>
<td>2</td>
<td>10(5)</td>
</tr>
<tr>
<td>CoOD⁺(2Σg) + D₂(2Σg)</td>
<td>1.96</td>
<td>0.667⁷</td>
<td>1</td>
<td>8(5)</td>
</tr>
<tr>
<td>Co⁺D⁻(2Σg) + OD(2Σg)</td>
<td>13.90</td>
<td>1.1²</td>
<td>1</td>
<td>32(10)</td>
</tr>
<tr>
<td>Co⁺(F⁻) + D₂O⁺(2Σg)</td>
<td>14.94</td>
<td>1.45²</td>
<td>2</td>
<td>35(5)</td>
</tr>
</tbody>
</table>


Intermediate, I, in this reaction system, while total angular momentum and energy are explicitly conserved. Because the common thresholds observed for reactions 7 and 8a suggest that there is an activation barrier due to the four-centered transition state in the entrance channel of this reaction system, additional assumptions must be added to PST. As we have outlined elsewhere,⁵⁶ we use a theory for translationally driven (TD) reactions as outlined by Chesnavich and Bowers,⁵⁸ who adapted a treatment of Marcus.⁵⁹

Table 3 lists the molecular constants for reactants and products used in this calculation, and Table 4 gives other parameters needed for the calculation. Molecular parameters for the four-centered CoOD₂⁺ transition state were taken from calculations by Fiedler et al.⁵¹ for the analogous four-centered transition state for the FeOH₂⁺ system. These calculations include results for both a high-spin and a low-spin transition state and both sets of parameters were tried in our calculations. Endothermicities for reactions 7 and 9 were taken as the literature values given above, and the exothermicity for reaction 8a was taken as 1.34 eV which is the energy for spin-allowed formation of the Co⁺(2F) excited state. The height of the transition-state barrier was allowed to vary to best reproduce the experimental cross sections. Another adjustable parameter in these calculations is the number of reactive surfaces. For the CoO⁺(2Δg) + D₂(2Σ_g) reactants, which have a total degeneracy of ten, the only reasonable choices are five and ten reactive surfaces with the former value giving better agreement with the experimental data.

The results of this TD-PST calculation are compared with the experimental data in Figure 8. These results were obtained by using parameters for the high-spin transition state. (Parameters for the low-spin species yielded cross sections with magnitudes much lower than experiment.) Without adjusting the parameters for the transition-state II or the reactants, theory is easily able to reproduce the absolute magnitude and shape of the total cross section up to about 2 eV. The only adjustable parameters being the number of reactive surfaces 5 and the barrier height, 0.65 ± 0.05 eV. Because this calculation assumes that only translational energy is used to cross the barrier, this barrier height should be compared with that measured above without including contributions from the internal energy of the reactants, namely 0.70 ± 0.04 eV. Note that this TD-PST calculation explicitly includes the possibility that the reactants fail to cross the barrier and that the strongly coupled intermediate can also dissociate by re-crossing the barrier. The good agreement between this calculation and our data confirms that there are no kinetic or competitive shifts influencing our results. It seems likely that similar conclusions hold for the methane system.

The phase space calculation is also found to reproduce the product branching ratios up to about 2 eV. The results shown in Figure 8 use an estimate for the rotational constant for CoOD⁺ of 1.1 cm⁻¹, somewhat reduced from our initial estimate of 1.3 cm⁻¹. This change increases the density of states for this channel but does not affect the total cross section for reaction. Alternatively, reasonable agreement could be achieved by invoking an exit channel barrier for elimination of D₂O from intermediate I, a possibility discussed above. In this model, the optimum energy for such a barrier was about 0.8 ± 0.2 eV relative to the CoO⁺ + D₂ reactants. The observation that the TD-PST calculation can reproduce the experimental cross sections of all channels with reasonable fidelity implies that the assumptions of this calculation hold; namely, the reaction proceeds by passing over...
a tight transition state at low energies, and then forming a strongly coupled intermediate that dissociates statistically into the three observed channels.

Above 2 eV, the TD-PST calculation deviates from the experimental data. Note that the calculation overestimates the amount of CoOD+ + D and underestimates the amount of Co+ + D2O, suggesting that the branching ratio is no longer controlled by statistical factors alone at these elevated kinetic energies. Indeed, the experimental data can be rationalized by noting that as the energy increases, the lifetime of the intermediate becomes shorter, thereby decreasing the time available to randomize energy in all degrees of freedom. In such circumstances, angular momentum conservation becomes increasingly important. Because the reduced mass of the CoOD+ + D products is less than that of the reactants and much less than that for the Co+ + D2O channel, Table 4, the latter channel will be favored by angular momentum considerations while the former will be disfavored.

Summary

Cross sections for the reactions of Co+ + D2O, CoO+ + D2, Co+ + CH3OD, CoO+ + CH4, and Co+(CH3OD) + Xe are reported. The most intriguing observation is that the oxidation of methane and D2 by CoO+, both exothermic reactions, does not occur until overcoming activation barriers of 0.56 ± 0.08 and 0.75 ± 0.04 eV, respectively. The behavior of the forward and reverse reactions in both the D2 and CH4 systems is consistent with reactions that proceed via the insertion intermediates R–Co–OH, where R = CH3 or H. Molecular orbital ideas suggest that the activation barrier is likely to correspond to a four-centered transition state associated with addition of RH across the CoO+ bond. Reasonably detailed potential energy surfaces for both reaction systems are derived from the experimental data. Although the low-lying electronic states of CoO+ are unknown, they are likely to influence the reaction dynamics and likely possibilities are discussed in some detail. Phase space theory calculations for the CoO+ + D2 reaction help confirm details of the proposed mechanism and potential energy surfaces.

Analysis of endothermic thresholds for production of CoD+, CoH, and CoCH3+ leads to thermochemistry consistent with previous studies in our laboratory and that for CoOH+ and CoOCH3+ is consistent with work in other laboratories. Thermochemistry for Co+(CH3OH) and the OCoCH3+ isomer is derived here for the first time.

Acknowledgment. This work is supported by the National Science Foundation, Grant CHE-9221241. We thank D. Schröder and H. Schwarz for communicating results before publication and for drawing our attention to the question of a kinetic shift.