Stoichiometric Gas-Phase Oxidation Reactions of CoO^+ with Molecular Hydrogen, Methane, and Small Alkanes

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Fourier-transform ion cyclotron resonance mass spectrometry has been used to study the gas-phase reactions of CoO^+ with dihydrogen, methane, ethane, propane, and the isomers of butane and pentane. The cobalt oxide cation CoO^+ was generated from the reaction of Co^+ (produced by laser desorption) with N_2O, producing CoO^{+*}, which was subsequently thermalized by collisions with argon buffer gas. The activation of methane by CoO^+ results in the very inefficient exothermic formation of CH_3OH. Ethane through pentane are much more reactive toward CoO^+ as compared to methane. Ethane reacts by eliminating water, ethylene, and ethanol. For propane and larger alkanes activation of the carbon backbone is also observed. The cobalt–butadiene cation is the major product ion from the reaction of *n*-butane and is generated as well from *n*-pentane and 2-methylbutane. Branched alkanes display more complicated reaction pathways, including carbocation formation. Isotopic labeling experiments using CH_3CD_3, $CH_3CD_2CH_3$, $CH_3CH_2CD_2CD_3$, and $(CH_3)_3CD$ were used to reveal details concerning the specificity of C—H and C—C bond activation processes for ethane, propane, butane, and 2-methylpropane. Generally, the increased reactivity of CoO^+ relative to Co^+ can be explained by favorable exothermicities of the oxidation products eliminated, i.e. alcohols, alkenes, and water.

Introduction

Transition-metal-mediated functionalization of methane and other small hydrocarbons constitutes a fundamental topic of chemical activation.[1] Paramount in these studies are oxidation reactions of hydrocarbons which are not only economically attractive but also represent a bold scientific challenge. Oxygen atom transfer reactions catalyzed by transition-metal complexes have been studied extensively,[1,2] yet relatively few studies exist concerning gas-phase oxidation processes.[3–5] Gas-phase studies have great potential for revealing intrinsic reaction features in the transformations of metal-complex cations and for gaining further insight into fundamental processes of metal-catalyzed oxidations. This information is essential for developing new experimental approaches to meet present scientific challenges. For example, the search for more efficient catalysts for the conversion of methane to methanol has been listed as one of ten challenges for catalysis.[2e] Further, the number of empirically developed reagents and catalysts for oxidation of important fuel stocks has outpaced the development of models for understanding the reaction processes necessary for improving catalytic efficiencies. Salient information of the interactions of ionic transition-metal oxides with organic substrates, acquired through gas-phase investigations, may eventually lead to significant modifications in applied organometallic catalysis.

Cobalt compounds are commonly used as industrial catalysts for oxidation processes by using molecular oxygen or peroxides, for example, as terminal oxidants.[2,6] However, not too much is known with regard to their specific catalytic activity or the reaction intermediates; this knowledge is needed for detailed mechanistic investigations aimed at a tailor-made design of catalysts. Coordinatively unsaturated cobalt–oxide species have been implicated as active participants in selected olefin-oxidation reactions; however, due to the reactivity of ephemeral intermediates, the characterization of crucial reaction steps remains elusive.[6,7] In our continuing effort to examine and understand oxidation

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processes of organic substrates mediated by transition-metal oxide cations,[8-11] we now report the reactions of gas-phase CoO^{+} with small alkanes and molecular hydrogen investigated by using *Fourier* transform ion cyclotron resonance mass spectrometry (FTICR).

Previous reports concerning reactions of FeO^{+} [8-10,12] and CrO^{+} [13] with alkanes have demonstrated the variety of processes that are observable in the gas phase for these metal oxides. Of particular interest is the activation of methane by FeO^{+}, which was reported to occur through four possible reaction intermediates necessary to account for the measured product distribution.[8b] Another relevant example for gas-phase catalytic oxidation is the FeO^{+}/ethane system, which passes through an evident $Fe(H_2O)(C_2H_4)^{+}$ intermediate before proceeding to products.[9a,12]

Considerable progress has been made concerning the reactions of bare Co^{+} with organic molecules,[14-26] and this work serves as a model for the CoO^{+} studies. As will be shown, the noticeable differences in the reactivity of the cobalt and cobalt oxide cations are due to the enhanced reactivity of CoO^{+}, especially its ability to activate methane and ethane, which are unobserved processes for Co^{+} at thermal energies.[21]

Results and Discussion

Table 1. Product Distributions[a] and Estimated Reaction Enthalpies ($\Delta H_r°$ in kcal mol^{-1})[b] for Reactions of Co^{+} and CoO^{+} with Selected Linear Alkanes

	Co^{+} [c]			CoO^{+}		
substrate	neutral eliminated	branching ratio	$-\Delta H_r°$	neutral eliminated	branching ratio	$-\Delta H_r°$
methane	NR			CH_3OH	1.0	14
ethane	NR			H_2O	0.67	53
				C_2H_5OH	0.21	9
				C_2H_4	0.12	49
propane	H_2	0.59	16[d]	H_2O	0.73	58
	CH_4	0.41	24[d]	C_3H_7OH	0.16	12
				CH_3OH	0.06	38
				C_3H_6	0.05	52
n-butane	C_2H_6	0.59	21	H_2O; H_2	0.67	28
	H_2	0.29	34[d]	C_2H_4; H_2O	0.20	51
	CH_4	0.12	30[d]	CoOH	0.09	15[e]
				C_4H_8	0.04	52
n-pentane	C_2H_6	0.60	26	C_2H_5OH	0.43	46
	H_2	0.30	23[d]	CH_4; H_2O	0.20	41
	C_3H_8	0.08	21	CoOH	0.14	20[e]
	CH_4	0.02	36[d]	C_3H_8O	0.12	41
				H_2O	0.07	63[d]
				C_5H_{10}	0.04	52

[a] Product distributions are given as branching ratios. [b] $\Delta H_f°$ data for neutral molecules are taken from ref 27. The $\Delta H_f°$ values for LCo^{+} species (L = organic ligand) are taken from several literature sources. See text for details. [c] Reference 21. [d] The $\Delta H_f°$ values were derived by using data given in ref 14. [e] This work.

Table 2. Product Distributions[a] and Estimates of Reaction Enthalpies ($\Delta H_r°$ in kcal mol^{-1})[b] for Reactions of Co^{+} and CoO^{+} with Selected Branched Alkanes

	Co^{+} [c]			CoO^{+}		
substrate	neutral eliminated	branching ratio	$-\Delta H_r°$	neutral eliminated	branching ratio	$-\Delta H_r°$
2-methylpropane	CH_4	0.77	24[d]	CoOH	0.30	15[e]
	H_2	0.23	16[d]	C_4H_9OH	0.20	20
				H_2O; H_2	0.18	
				CH_3OH	0.16	41
				H_2O	0.16	33[d]
2-methylbutane	CH_4	0.39		C_2H_5OH	0.40	41
	C_2H_6	0.28	24	CH_4; H_2O	0.30	36
	H_2	0.21		CoOH	0.30	20[e]
	C_3H_8	0.05	19			
	H_2; CH_4	0.05				
	$2H_2$	0.02				
neopentane	CH_4	1.00		$CoCH_3O$	0.64	
				"CH_5O"	0.10	
				CH_3OH	0.10	44[d]
				CH_4; H_2O	0.04	
				CoOH	0.04	20[e]
				CoC_2H_5O	0.04	
				C_3H_8O	0.02	38
				H_2O; H_2	0.02	

[a] Product distributions are given as branching ratios. [b] Enthalpy data were taken from ref 27 unless noted otherwise. The value of $\Delta H_f°(CoC_2H_4)^{+}$ was taken from ref 15. [c] Reference 21. [d] The $\Delta H_f°$ values were derived by using data from ref 14. [e] This work.

Branching ratios for the reactions of CoO^{+} with hydrocarbons examined in this work are given in Tables 1 and 2, and rate constant data for selected reactions are given in Table 3. Thermodynamic data for organic substrates used to determine reaction enthalpies ($\Delta H_r°$) were taken from ref 27. Specific mention is given to sources used for the estimates of heat of formation, $\Delta H_f°$,

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Table 3. Rate Constant Data for Selected Reaction Couples[a]

couple	k_f	k_f/k_C[b]
CoO^+/CH_4	0.05	0.005
CoO^+/C_2H_6	5.1	0.5
CoO^+/C_3H_8	5.6	0.5
$CoO^+/n\text{-}C_4H_{10}$	14	1.2
$CoO^+/i\text{-}C_4H_{10}$	4.8	0.4
$CoO^+/n\text{-}C_5H_{12}$	10	0.8
$CoO^+/i\text{-}C_5H_{12}$	7.5	0.6
$CoO^+/C(CH_3)_4$	11	0.9

[a] Pseudo-first-order rate constants are reported in units of 10^{-10} cm^3 molecule^{-1} s^{-1} with ±30% experimental uncertainty except for the CoO^+/CH_4 couple (±100%). [b] The capture collisional rate constants, k_C, were determined as previously described: Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

for ligated cobalt ions. In the discussions concerning reaction thermochemistry, usually the energetically most stable neutrals are presumed to be involved, although other combinations may be possible, unless data suggest otherwise. For example, "CH_6O" elimination is inferred to be methane/water ($\sum\Delta H_f^\circ = -76$ kcal/mol^{-1}) rather than methanol/dihydrogen ($\sum\Delta H_f^\circ = -48$ kcal/mol^{-1}) or $CH_2O/2H_2$ ($\sum\Delta H_f^\circ = -26$ kcal/mol^{-1}). This is purely a thermochemical argument and in no way serves as the only means for interpreting the observed reactivity.

The organization of this paper is as follows. Prior to the discussion of the reactions of CoO^+ with alkanes and molecular hydrogen, the production of the cobalt oxide cation will be considered with reference to the salient literature. Then the reactions of CoO^+ with methane, ethane, propane, *n*-butane, and 2-methylpropane are discussed in detail, and mechanistic insight is provided by isotopic labeling studies, by collision-induced dissociation (CID) and double-resonance (DR) experiments, and by examining variations in the reaction precursors. The reactions of isomeric pentanes are then considered. Additionally, from the reactivity studies of CoO^+ with various alkanes, an upper limit for the Co—OH bond strength is derived. Finally, we return to the CoO^+/H_2 system as a basic model for transition-metal-mediated oxidation. A preliminary report of the surprisingly low reactivity of CoO^+ with H_2 has been published recently,[11a] and further features of this seemingly simple system are presented here.

Production and Thermalization of the Cobalt–Oxide Cation. Kappes and Staley initially examined the oxidation of Co^+ by N_2O and O_2 by using ion cyclotron resonance mass spectrometry (ICR);[3a] however, they did not observe CoO^+ under thermal conditions from either precursor, indicative of endothermic processes or exothermic reactions which are prohibited due to large kinetic barriers. Armentrout and coworkers have also examined the same systems by using guided ion beam mass spectrometry.[3b,c] It was observed in their studies that the formation of CoO^+ from Co^+ and O_2 (eq 1) is indeed endothermic, and the bond dissociation energy has been determined ($D^\circ(Co^+{-}O) = 75.9 \pm 1.4$ kcal mol^{-1}).

$$Co^+ + O_2 \rightarrow CoO^+ + O \qquad (1)$$

The nonoccurrence of the oxygen atom transfer reaction of Co^+ with N_2O (eq 2) has been attributed to a kinetic barrier due to curve crossing to satisfy the spin conservation of cobalt cation to the cobalt oxide cation along the potential energy surface,[3b] albeit eq 2 is exothermic by 40 kcal mol^{-1}. Another example concerns

$$Co^+ + N_2O \rightarrow CoO^+ + N_2 \qquad (2)$$

the thermal decomposition of N_2O to N_2 and O, which proceeds via curve crossing and is associated with an activation energy (E_a) of 62 kcal mol^{-1}.[28] Similarly, the exothermic oxygen atom transfer reactions involving N_2O with the metal ions Cr^+, Mn^+, and Ni^+ are also impeded due to the presence of activation barriers for these reactions.[3a,b]

The relatively large reaction pressures of ca. 1×10^{-6} mbar prevailing in the earlier ICR study would result in efficient thermalization of electronically excited bare metal ions and, thus, even exothermic reactions would not be observed if an activation barrier is present in excess of the energy of the entrance channel.

In the present study, because of the low yields of CoO^+ obtained from reaction 2 at thermal energies, N_2O was allowed to react with translationally or electronically excited Co^{+*}. Therefore, CoO^+ was generated via translational excitation of Co^+ by applying a radiofrequency excitation pulse focused at Co^+ to initiate a collision-induced reaction with N_2O.[3b,c] In addition, the reaction of electronically excited Co^{+*}, produced from laser desorption, may also contribute to the formation of CoO^+. The excited-state population of Co^+ is dependent on accessible high-energy states of Co^+, and at $T =$ 2000 K ca. 20% corresponds to the ^5F state,[29] which lies 0.41 V above the ^3F ground state of Co^+.[30] Interestingly, the excited-state population of Co^{+*} is also dependent upon the choice of Co precursor;[25] in the present work a solid metal target was exclusively used. The extent of translational excitation is not unlimited, because at high kinetic energies it will result in CID of the product or even approach ion ejection energies rather than ion activation; consequently, the absolute yield of CoO^+ will decrease although yields with respect to Co^+ will increase. Total conversion of Co^+ to CoO^+ was not achieved, since ion selection, ion ejection, and quenching processes as well as the reaction of interest compete with each other and the optimal conversion ratio of Co^+ to CoO^+ was ca. 20%. An explicit differentiation between the ground-state and excited-state populations is not always straightforward by using FTICR, and thus, quantifying the production of CoO^+ from either translational or electronic excitation is a prodigious undertaking. Consequently, the population of CoO^{+*} initially formed in reaction 2 is believed to contain ions in an vibrationally excited ground-state distribution.

The excited CoO^{+*} ions were quenched by collisional cooling with buffer gases prior to reaction with RH substrates (R = alkyl or hydrogen). Several buffer gases were studied in order to qualitatively evaluate the thermalization efficiency of "hot" CoO^{+*} ions. Thorough thermalization was evaluated by the reproducibility of reaction kinetics and the nonoccurrence of endoergic reactions, such as the absence of the formation of

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$CoOH^+$ in the reaction of CoO^+ with methane (see below). Although xenon, krypton, and SF_6 are more massive than Ar and N_2, for example, all buffer gases were effective and resulted in rapid and evidently complete thermalization of any translational or internally excited CoO^{+*} ions produced in reaction 2.

Activation of Methane by CoO^+. Methane activation mediated by CoO^+ proceeds through the elimination of neutral CH_4O (inferred to be methanol) as shown in eq 3 with $\Delta H_r^\circ = -14$ kcal mol^{-1}.

$$CoO^+ + CH_4 \rightarrow Co^+ + CH_3OH \qquad (3)$$

At thermal energies reactions involving bare Co^+ with methane are not observed and the reaction described in eq 3 is presumably driven by the elimination of a stable neutral.[21] Indicative that in our reaction conditions we employ thermal CoO^+ cations is the observation that the cobalt–hydroxide cation $CoOH^+$ is not observed (eq 4), which is expected to be an endothermic process

$$CoO^+ + CH_4 \rightarrow CoOH^+ + CH_3^\bullet \qquad (4)$$

($\Delta H_r^\circ = 6 \pm 4$ kcal mol^{-1}). This argument is supported by the fact that methyl radical elimination can indeed be observed, if CoO^+ is not thoroughly thermalized.

The forward rate constant for methane activation by CoO^+ ($k_f \approx 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) measured under FTICR conditions is quite inefficient as compared to that for FeO^+ ($k_f = 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1});[8a] thus, C—H bond activation of methane by CoO^+ occurs approximately once every 200 collisions as estimated from the Langevin collision theory. Evaluation of an intermolecular kinetic isotope effect using CD_4 is not practical, considering the large experimental uncertainty of the rate constants for reactions depicted in eqs 3 and 5.

$$CoO^+ + CD_4 \rightarrow Co^+ + CD_3OD \qquad (5)$$

A recent guided ion beam mass spectrometric (GIBMS) study[31] of the CoO^+/CH_4 system maintains that reaction 3 occurs with a threshold of 0.6 eV. This indicates that methane oxidation mediated by CoO^+ is not a thermal process but possesses an activation barrier which exceeds the entrance channel; further, this would indicate that the CoO^+ ions produced under our experimental conditions are either not completely thermalized or electronically excited. Another point of contention in the GIBMS study[31] is that the cross section for reaction 4 is larger than that of eq 3,[31] which is exothermic. It should be noted that the ΔH_r° value for eq 4 is based on the Co^+—OH bond strength (BDE = 71 ± 3 kcal mol^{-1})[32] and the Co^+—O bond strength (BDE = 76 ± 1 kcal mol^{-1})[3c] and, thus, includes an experimental uncertainty which is in the order of magnitude of the predicted reaction endothermicity.[33]

According to our results, eq 3 is indeed an exothermic, thermal process and does not possess a significant threshold which would prohibit methanol formation. This presumption is supported by the following facts and observations. (i) Co^+ formation can be followed for several half-lives and the decay of CoO^+ displays pseudo-first-order kinetics (Figure 1). For eq 3 to proceed to such an extent requires either that almost all CoO^+ ions are internally or translationally excited, which seems unlikely, or that the reaction is not totally prevented by a kinetic barrier, thus proceeding also with ground state CoO^+. However, the low efficiency of reaction 3 indicates that the activation barrier is close to the energy of the entrance channel. In addition, the participation of electronically excited CoO^+ is improbable, since there is no reason why excited CoO^{+*} should not undergo reaction 4, which would be exothermic for CoO^{+*}. (ii) A recent theoretical account[5] indicates that the first excited state of CoO^+ lies ca. 1 eV above the ground state. Thus, at 300 K essentially 100% of the CoO^+ ions are in the ground electronic state. Additionally, at 300 K, the Boltzmann distribution of methane molecules possessing enough kinetic energy to overcome the 5 kcal/mol threshold derived for eq 3 from the GIB study[31] is insignificant. (iii) CoO^+ was trapped in 1×10^{-7} mbar argon for 100 s (corresponding to ca. 200 thermalizing collisions) in the absence of methane; however, Co^+ was not observed, indicating that the reactions with background contaminants are negligible. Performing the same experiment with subsequent introduction of methane after the 100 s trap produces cobalt cations, indicative that O atom transfer from CoO^+ to methane has occurred. Because of the purity of the methane used in this work (see Experimental Section), it is unlikely that the reagents supply a source of possible contamination. In addition, the most likely impurities in commercial methane are air, water, or ethane. Air and water are unreactive toward CoO^+, and ethane would also yield $Co(C_2H_4)^+$ (see below), which is not observed experimentally.

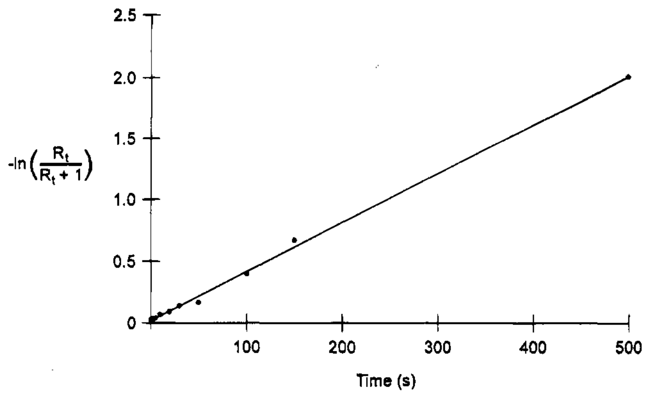

Figure 1. Pseudo-first-order kinetic data for eq 3. $R_t = [CoO^+]/[Co^+]$ at time t(s) and $p(CH_4) = 6 \times 10^{-8}$ mbar as previously described: Richardson, D. E.; Christ, C. S.; Sharpe, P.; Eyler, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3894. See text for further details.

Possible sources of error for both the FTICR and the GIBMS experiments should also be considered. Because of the small cross sections observed in the GIBMS work, it is possible that kinetic shifts may bias signal detection. Further, the small cross sections reach the experimental limits of measurability and inherently have considerable experimental uncertainties. Similarly for the FTICR studies, highly inefficient reaction processes will also have large experimental uncertainties in the rate constants. In conclusion, it cannot be absolutely ruled out that the formation of Co^+ observed under the conditions of FTICR has a different origin than de

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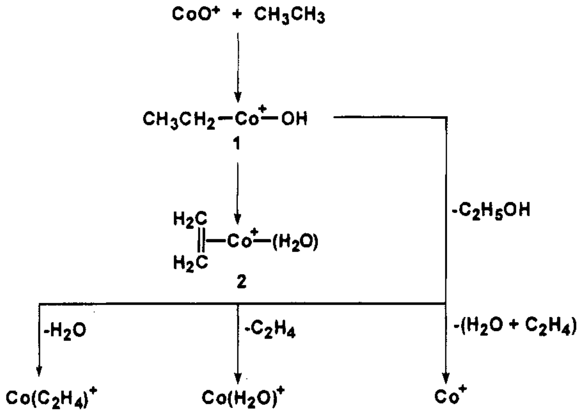
(31) Chen, Y.-M.; Clemmer, D. E.; Armentrout, P. B. *J. Am. Chem. Soc.*, in press.

(32) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 6176.

Scheme 1



scribed in eq 3. Although careful steps were taken to refute this possibility (see above), because we lack the ability to screen all components that constitute background impurities, we are left to presume that oxidation of methane occurs, albeit inefficiently.

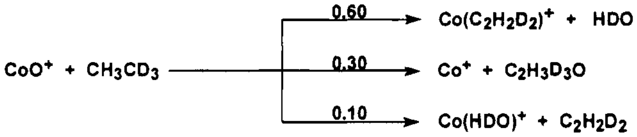
Reaction with Ethane. In contrast to the CoO^+/methane system, the reaction of CoO^+ with ethane is quite efficient (Table 3). Water loss is the most exoergic process (Table 1) and is observed to the greatest extent in the reaction of CoO^+ with ethane; the complementary evaporation of C_2H_4 accompanied with $Co(H_2O)^+$ production is much less intense despite the large exothermicity of this reaction channel. Additionally, Co^+ is formed with the simultaneous generation of C_2H_6O (presumably ethanol). The reactivity of CoO^+ is in sharp contrast to that of bare Co^+, which does not react at all with ethane at thermal energies although an exothermic dehydrogenation channel exists.[21] For CoO^+, all three processes are strongly exothermic and can be accounted for by invoking a common intermediate **1** (Scheme 1), as previously suggested by Freiser and coworkers for FeO^+/ethane:[12] insertion of the CoO^+ ion into a C═H bond, followed by β-hydrogen transfer, generates the cobalt aquo ethylene cation (**2**), which subsequently can either elminate water, ethylene, or both. Water loss is preferentially observed over ethylene elimination, in agreement with the relative bond strengths BDE(Co^+—C_2H_4) = 43 kcal mol^{-1} [15] and BDE(Co^+—OH_2) = 40 kcal mol^{-1}.[34] Formation of ethanol can be inferred from reductive elimination from **1** rather than a water/ethylene combination from **2**; on the basis of the thermochemistry, however, either process is strongly exothermic.

For comparison, the reaction of bare Co^+ with ethanol proceeds with ethylene and water elimination and these channels are consistent with the products observed for the CoO^+/C_2H_6 reaction.[17] In a search for further intermediates, dimethyl ether was reacted with Co^+ and was found to form exclusively $Co(OCH_2)^+$ (eq 6). As this

$$Co^+ + CH_3OCH_3 \rightarrow Co(OCH_2)^+ + CH_4 \qquad (6)$$

product is not observed in the reaction of CoO^+ with ethane, initial C—C bond insertion to yield $[CH_3CoOCH_3]^+$ is not involved in the CoO^+/C_2H_6 system; similarly, C—C bond activation does not occur in the reaction of FeO^+ with ethane.[12]

Scheme 2



The intermediacy of the insertion product **1** is supported by reacting CoO^+ with CH_3CD_3 (Scheme 2). From the CoO^+/ethane encounter complex, the neutral molecules HDO, $C_2H_3D_3O$, and $C_2H_2D_2$ are evaporated with no evidence in support of other isotopologues. This clearly demonstrates that each methyl group delivers one (and only one) hydrogen/deuterium atom to the metal center. Hydrogen/deuterium atom exchange processes are not observed within the experimental uncertainty (<5%). Also notable is that the branching ratios for the reactions of CoO^+ with C_2H_6 and $C_2H_3D_3$ are almost constant for ethylene and water losses, being in line with the genesis of the central intermediate **2**. The slight increase in the formation of Co^+ (0.21 in the CoO^+/C_2H_6 system and 0.30 in the CoO^+/CH_3CD_3 system) is in keeping with the reductive elimination of ethanol from **1** instead of consecutive losses of ethylene and water from **2**.

Studies involving the intermediates depicted in Scheme 1 were performed to further our understanding of the oxidation processes involving fundamental organometallic species. Oxidation of $Co(H_2O)^+$ by N_2O predominantly generates $Co(OH)_2^+$ (eq 7). This process is very

$$Co(OH_2)^+ + N_2O \rightarrow Co(OH)_2^+ + N_2 \qquad (7)$$

$$Co(C_2H_4)^+ + N_2O \rightarrow Co^+ + C_2H_4O + N_2 \qquad (8)$$

exothermic (ΔH_r° = ca. -35 kcal mol^{-1}) and proceeds relatively quickly with $k_f = 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Previously, the corresponding $Fe(OH)_2^+$ cation was proposed to constitute a sink in the catalytic oxidation of ethane by FeO^+.[9] In the latter system the rapid oxidation of $Fe(H_2O)^+$ by N_2O ($k_f = 6.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) competes with the oxidation of $Fe(C_2H_4)^+$ by the same oxidant ($k_f = 0.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}), resulting in a limited turnover number for the iron catalyst.[9] For the corresponding cobalt system studied here, the oxidation of $Co(C_2H_4)^+$ was also observed to be slow relative to the oxidation of $Co(H_2O)^+$ (eq 8; $k_f = 0.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and may reflect the absence of a significant thermodynamic driving force or a significant kinetic barrier. If C_2H_4O corresponds to ethylene oxide elimination, $\Delta H_r^\circ = -1$ kcal mol^{-1} is estimated for eq 8, while -27 kcal mol^{-1} is liberated if acetaldehyde is formed as the neutral product. The $Co(C_2H_4O)^+$ cation is not observed in significant yields under our experimental conditions; thus, structural information concerning this species could not be assessed by CID. Nevertheless, previous investigations indicate that $[FeC_2H_4O]^+$ most likely corresponds to a metallaoxacyclobutane[7c,9] and, analogously, the $Co(C_2H_4O)^+$ species may be presumed to correspond to a metallacycle as well.

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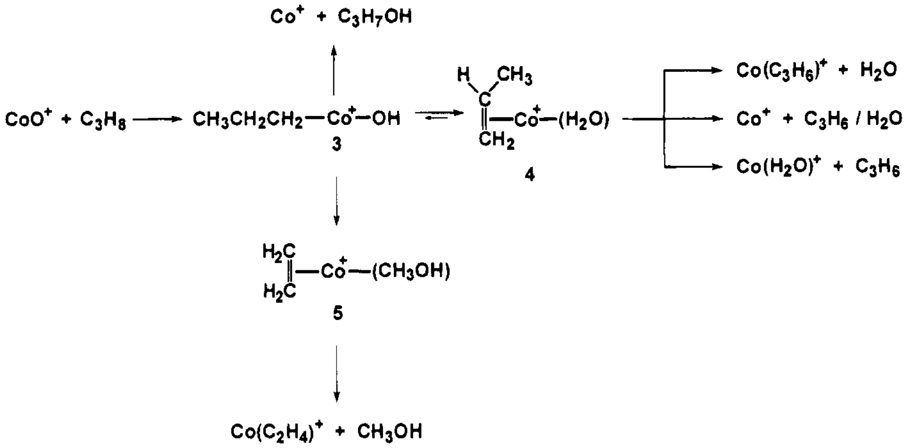
(33) As the Co—CH_3 bond is weaker than the Co^+—OH bond (61 kcal mol^{-1} [21] versus 71 kcal mol^{-1} [31]), the species $Co(OH)(CH_3)^+$ is indeed expected to decompose to $CoOH^+$ rather than $CoCH_3^+$.

(34) Marinelli, P. J.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 4101.

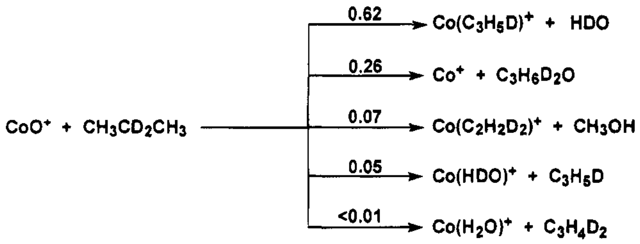
Scheme 3



Reaction with Propane. The reaction of Co^+ with propane has been studied in detail.[14,20-22,24,25,35] Propane is of interest because it is the smallest alkane to react with Co^+ (as well as Fe^+ and Ni^+) at thermal energies, undergoing both C—H and C—C bond activation.[14,20,24] The pseudo-first-order rate constant for the CoO^+/propane couple is slightly greater than that measured for ethane, in keeping with the increased polarizability of propane. Bare Co^+ reacts with propane with a much slower rate constant ($k_f = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}), which has been attributed to the formation of a tight transition state from the $Co(C_3H_8)^{+*}$ encounter complex.[24,25b] The state-specific reactions of $3d^7\,4s^1$ Co^+ (^5F and/or ^3F) with propane show a considerable increase in chemical reactivity, i.e. insertion/elimination channels, relative to the ground-state $3d^8$ Co^+ (^3F) cation ($k_f(3d^7\,4s^1)/k_f(3d^8) = 6.2$).[25] For ground-state Co^+, C—H bond activation, resulting in the elimination of H_2, is observed to a greater extent over the energetically more favored methane elimination pathway.[20,24] Similarly, the product of C—H bond activation, i.e. H_2 loss, dominates as compared with products resulting from cleavage of C—C bonds.

Although propene elimination is almost as exothermic as water elimination, similar to the olefin loss from ethane, it is the least important reaction pathway in the CoO^+/C_3H_8 system. On the basis of the argument of competitive bond dissociation energies, H_2O elimination is preferred since BDE(Co^+—propene) = 53 kcal mol^{-1},[24] which exceeds BDE($Co^+—OH_2$) = 40 kcal mol^{-1}.[34] Double-resonance experiments on the Co^+ product ion revealed a slight effect for the $Co(C_2H_4)^+$ complex, indicating that, over long reaction times, a secondary reaction of Co^+ with propane occurs. Similar experiments were performed for the reactions of CoO^+ with butanes and pentanes (see below), and the reported branching ratios have been corrected for the effects of secondary reaction processes.

Scheme 4



The reaction of CoO^+ with $CH_3CD_2CH_3$ helped to establish a reaction mechanism, and an oversimplified description is outlined in Scheme 3. The reaction products and the branching ratios shown in Scheme 4 are in line with an C—H bond activation at a primary carbon as the first step in the reaction sequence to generate the central intermediate **3**, from which all products can emerge in a straightforward manner. The loss of HDO to yield $Co(C_3H_5D)^+$ is observed with ca. 10% H/D scrambling, thus indicating that isomerization between **3** and **4** is reversible but slow; however, loss of D_2O was below the detection limit. Similarly, the complementary loss of propene is associated with a small amount of H/D exchange processes, as indicated by the formation of $Co(H_2O)^+$, whereas again $Co(D_2O)^+$ could not be detected. A methyl shift from **3** to generate **5**, presumably in a multistep sequence, is supported by the formation of $Co(C_2H_2D_2)^+$ as the exclusive ethylene complex; alternatively, **5** can also be generated via an initial C—C bond activation step. A distinct kinetic isotope effect is discernible for HDO (62%) elimination in the $CoO^+/CH_3CD_2CH_3$ system relative to H_2O loss (73%) for the $CoO^+/CH_3CH_2CH_3$ system in favor of the competition for Co^+ formation. This indicates that formation of Co^+ is indeed accompanied by reductive elimination of propanol from **3** rather than elimination of propene/water via **4**, since the reductive elimination channel is not associated with a primary kinetic isotope effect, whereas a primary H/D isotope effect is operative in the formation of **4**. As far as losses of water and ethylene are concerned, we cannot distinguish between an initial activation of a primary or a secondary C—H bond; however, if the initial C—H bond activation step were to occur at the secondary carbon to yield the $(CH_3)_2CD—CoOD^+$ intermediate, CH_3OD loss from an α-methyl shift would have to occur; this is not the case. Thus, it is plausible to assume that C—H bond activation commences at the methyl groups, despite the somewhat larger bond strength of a primary C—H bond.

Labeling studies concerning the reaction of bare Co^+ with propane also point to an initial C—H bond activation step at a terminal carbon to generate an intermediate similar to **3**.[24] For example, in the reaction of Co^+ with $CH_3CD_2CH_3$, HD and CH_4 losses account for ca.

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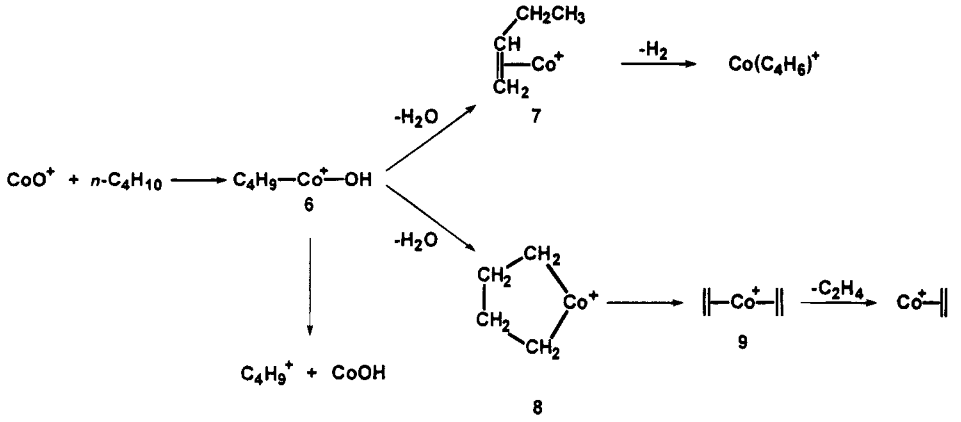
[35] Tonkyn, R.; Ronan, M.; Weisshaar, J. C. *J. Phys. Chem.* **1988**, *92*, 92.

Scheme 5



90% of the elimination products. Interestingly, the extent of increasing deuteration at the central carbon corresponds to an increase in the ratio of methane/hydrogen loss for the Co^+/propane couple. The data for CoO^+ indicate a similar trend, although the experimental uncertainty is larger due to the relatively small amount of methanol being formed. In a related study,[17,18] it was shown that *n*-propanol is dehydrated by Co^+, with propene elimination as a minor product.[18] Experiments of Co^+ with various *n*-propanol isotopomers also provide evidence for the operation of a methyl transfer from the 3-position to the metal center. For example, $CD_3CH_2CH_2OH$ exclusively eliminates CD_3OH via a cationic $CD_3{-}Co(OH)(C_2H_4)^+$ intermediate to generate $Co(C_2H_4)^+$, which supports the suggested formation of **5** in the course of the reaction of CoO^+ with propane.[18]

Reactions with *n*-Butane and 2-Methylpropane. Reactions of CoO^+ with large alkanes, especially the branched derivatives, become more complicated as compared to the smaller homologues. In particular, initial C—H activation may lead to the formation of intermediate carbocations in which facile rearrangements can occur, resulting in a manifold of products. The main product in the CoO^+/*n*-butane reaction is $Co(C_4H_6)^+$, presumed to be the cobalt—butadiene cation; similarly, butane reacts with FeO^+ and CrO^+ to form M^+—butadiene as the most abundant product ions.[13] Interestingly, the primary products of water loss, i.e. M^+—butene complexes, are not observed and the direction formation of M^+—butadiene cations may be the result of the dissipation of excess energy of the activated MO^+—hydrocarbon complex as well as the high reaction exothermicity by multiple evaporative neutral losses.[12] This supposition is further supported by the work of Tsarbopoulos and Allison, who studied the reactions of Co^+ with terminally substituted mono- and disubstituted *n*-butanes and in all cases observed $Co(C_4H_6)^+$ as the predominant product.[19] Other products of the CoO^+/butane system correspond to losses of water and ethylene, elimination of butene, and loss of neutral CoOH associated with charge transfer to the carbon to yield a carbocation (Table 1, Scheme 5).

Several likely reaction channels depicted in Scheme 5 were established for the CoO^+/*n*-butane system by using $CH_3CH_2CD_2CD_3$. Thus, after an initial C—H bond activation step to generate **6**, water loss can occur through either a 1,2-elimination or a 1,4-elimination channel to generate **7** or the metallacycle **8**, respectively. Dehydrogenation from **7** (or its 2-butene isomer) results in the formation of Co^+(butadiene). Here, the "extended" arm of the butene ligand is able to coordinate to the unsaturated metal center analogous to a chelate effect ("agostic interaction").[36] Although ΔS^* is negative for this process, and $-\Delta V^*$ values have been measured for similar effects,[37] the large overall exothermicity results in further dehydrogenation of butene to butadiene. The initial C—H bond insertion of the CoO^+ unit into a secondary C—H bond may also occur to form an *s*-butyl—Co^+—OH cation, which can then eliminate water and subsequently H_2 en route to the Co^+(butadiene) complex. As far as the labeling data are concerned, $Co(C_4H_3D_3)^+$ is formed as the major product associated with ca. 40% H/D exchange processes leading to $Co(C_4H_2D_4)^+$; thus, reversible 1,2-hydrogen migrations precede the consecutive losses of water and molecular hydrogen. The formation of a butyl cation from the reaction of CoO^+ with $CH_3CH_2CD_2CD_3$, forming either $C_4H_5D_4{}^+$ or $C_4H_4D_5{}^+$, is associated with an intramolecular kinetic isotope effect of $k_H/k_D = 1.03$. This indicates that the initial C—D bond insertion to form **6** (Scheme 5) is energetically equivalent to an initial C—H bond insertion process. With respect to the absence of carbocation formation in the reaction of CoO^+ with propane, the negligible primary kinetic isotope effect for CoOH and CoOD losses in the CoO^+/*n*-butane system can be rationalized by the formation of the energetically more stable *tert*-butyl cation as the ionic product and, thus, rearrangment of the carbon skeleton has to precede carbocation formation as the rate-determining step.

Further support for the mechanism depicted in Scheme 5, particularly the formation of the metallacycle **8**, is obtained from the formation of $Co(C_2H_4)^+$ and $Co(C_2D_4)^+$ (ratio 1:0.9) as the only ethylene complexes in the reaction of CoO^+ with $CH_3CH_2CD_2CD_3$. As this channel occurs without H/D scrambling and without a significant primary kinetic isotope effect, **7** and **8** cannot interconvert into each other within the experimental time scale. The reaction sequence for Co^+/ethylene formation may be explained as follows: 1,4-elimination of water forms **8**, which then rearranges to **9**, which subsequently loses ethylene. Formation of the bis(ethylene)cobalt cation **9** has also been invoked for the reaction of bare Co^+ with *n*-butane.[22]

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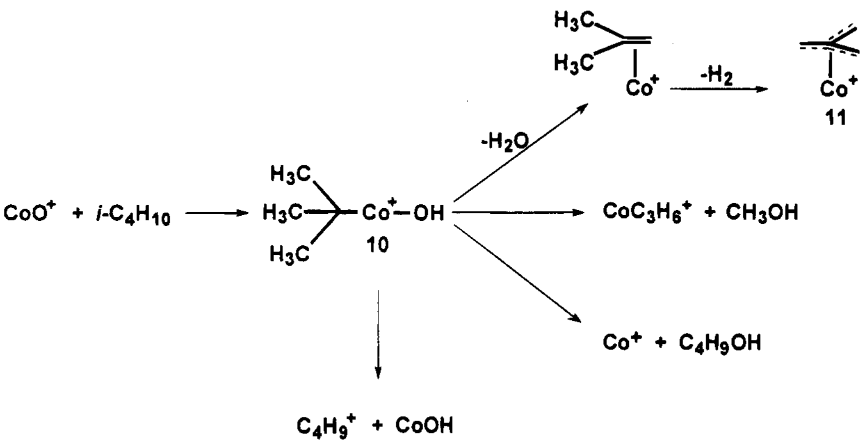
(36) For a definition and leading references on "agostic interactions", see: (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(37) Lawrance, G. A.; Stranks, D. R. *Acc. Chem. Res.* **1979**, *12*, 403.

Scheme 6



It is instructive to compare the Co^+/n-butane and the Co^+/n-butanol systems to the CoO^+/n-butane system.[17,19,22] The products for the bare metal species can be explained by a single mechanism:[18] in the Co^+/n-butanol system initial insertion of Co^+ to generate the $[n\text{-}C_4H_9—Co—OH]^+$ intermediate is followed by a hydrogen rearrangement and subsequent product formations, a mechanism analogous to that used here for the isomeric CoO^+/n-butane system. In a study by Armentrout and Beauchamp,[21] $Co(C_2H_4)^+$ was the most abundant product observed in the reaction of Co^+ with n-butane at thermal energies. This was later confirmed by the FTICR work of Jacobson and Freiser.[22] For comparative purposes, we studied the reaction of bare Co^+ with $CH_3CH_2CD_2CD_3$ and the products $Co(C_2H_4)^+$ and $Co(C_2D_4)^+$ were observed with no H/D scrambling as the most abundant ions in a 2:1 ratio. Here, a distinct difference between the reaction of bare Co^+ and its oxide congener becomes apparent: the formation of $Co(C_2H_4)^+$ from the reaction of Co^+ with n-butane has been explained via initial C—C insertion and subsequent β-H transfer, for which our measurement implies an H/D isotope effect of $k_H/k_D = 2.0$. In contrast, ethylene ligand loss from either **8** or **9** will not be subject to a primary H/D kinetic isotope effect, which is indeed borne out experimentally ($k_H/k_D = 1.1$). As a conclusion, initial C—H bond activation is favored for the oxide cation as compared to the bare metal, being in line with BDE(O—H) exceeding BDE(O—C).

Several differences are worthy of note in the reactions of Co^+ and CoO^+ with i-C_4H_{10}. For example, Co^+ dehydrogenates 2-methylpropane via 1,2-elimination consistent with an insertion/β-H transfer mechanism.[21] Moreover, HD loss was exclusively observed for the dehydrogenation in the reaction of Co^+ with $(CH_3)_3CD$. For CoO^+, also only $Co(C_4H_8)^+$ is formed from 2-methylpropane, as inferred from a similar labeling experiment using $(CH_3)_3CD$. Further, D loss accompanies all neutral eliminations. Thus, the $C_4H_9^+$ carbocation corresponds to a *tert*-butyl cation, resulting from CoOD elimination and not a primary carbocation, since CoOH loss was not observed at all. In addition, due to the fact that elimination of neutral cobalt hydroxide in the CoO^+/2-methylpropane system can occur without rearrangement of the carbon skeleton, it is not surprising that the amount of carbocation formation is 3 times larger than in the isomeric CoO^+/butane (see above). With respect to the loss of methanol, $Co(C_3H_6)^+$ is exclusively formed in the reaction of CoO^+ with $(CH_3)_3CD$. Thus, subsequent to the initial insertion into the C—D bond of the tertiary carbon (Scheme 6), methyl transfer irreversibly follows. Formally, the $Co(C_3H_6)^+$ so formed should exhibit a dimethylcarbene structure; however, it has been demonstrated that metal-mediated isomerization to the corresponding olefin complex is facile.[38]

The $Co(C_4H_6)^+$ species can either be the butadiene complex or, more likely, the intriguing trimethylenemethane (TMM) complex **11**. Formation of **11** requires less rearrangement and can be explained by extending the same mechanism as shown in Scheme 6: viz., insertion of Co^+ into a primary C—H bond of the $Co(C_4H_8)^+$ complex, followed by H transfer from a methyl carbon to eliminate H_2. Double-resonance experiments on $Co(C_4H_8)^+$ had no discernible effect on the intensity of $Co(C_4H_6)^+$, indicating that the H_2O/H_2 elimination is very rapid on the FTICR time scale. Because of the low yields of $Co(C_4H_6)^+$, CID experiments toward a distinction of both isomeric structures were not possible.

Reactions with *n*-Pentane, 2-Methylbutane, and 2,2-Dimethylpropane. n-Pentane reacts with CoO^+ to generate several products resulting from C—C and C—H bond activation step as well as the hydride-abstraction product CoOH (Table 1). Since a $C_4H_9^+$ ion is formed from the reaction of CoO^+ with n-butane, it is not surprising to observe the pentyl cation due to the lower ionization energy (IE) of the corresponding C_5H_{11} radicals. The majority of products generated from n-C_5H_{12} results from activation of the carbon framework, which may indicate an initial C—C bond insertion step, particularly since both ethanol and propanol eliminations are observed. Alternatively, if one assumes initial C—H bond activation, the loss of these alcohols would require an alkyl transfer to the metal center. Finally, methane/water elimination is also consistent with C—C bond activation resulting from an insertion in the $C_1—C_2$ position. The 1,2-insertion intermediate can eliminate either CH_3OH/H_2 or CH_4/H_2O.

The $Co(TMM)^+$ (**11**) product is possibly formed during the reactions of CoO^+ with 2-methylbutane and to a lesser extent, 2,2-dimethylpropane (neopentane). However, for the CoO^+/2-methylbutane reaction couple, the $Co(C_4H_6)^+$ product may also correspond to the cobalt—butadiene cation resulting from C—C bond activation at the tertiary carbon. Other proposed C_4 products

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[38] Schröder, D.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1994**, *116*, 5857.

observed for the reactions with neopentane are the η^3-methylallyl species and the Co^+ (2-methylpropane) complex. The product of interest for the neopentane reaction is the formation of $C_4H_9^+$, which is accompanied by the production of "$CoCH_3O$". Obviously, a methanide group is directly transferred to the approaching CoO^+, and the nature of the resulting neutral (i.e. $CoOCH_3$ or CH_3CoO)[31] remains to be established. The analogous hydride transfer to generate $C_5H_{11}^+$ is much less prevalent for *neo*-C_5H_{12} as compared with *i*-C_5H_{12}, reflecting the higher energy demand associated with the generation of an incipient primary carbocation.

The initial step required in several reactions described in the preceding sections corresponds to the insertion of CoO^+ into a C—H bond. Because of the importance of this step in developing viable reaction mechanisms and explaining the reactivity of CoO^+ toward hydrocarbons, we have attempted to derive an estimate for the Co—OH bond strength. From the larger alkanes studied here, we observe that carbocationic products give a lower limit for the CoOH ionization energy, i.e. IE(CoOH) > IE(t-C_4H_9) = 155 kcal mol^{-1},[27] leading to an estimate for BDE(Co—OH) > 43 kcal mol.

Activation of Molecular Hydrogen. Reaction 9 is quite inefficient ($k_f = 1.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}), considering the favorable thermochemistry ($\Delta H_r{}^\circ = -42$ kcal mol^{-1}) for this process. Also of interest is the

$$CoO^+ + H_2 \rightarrow Co^+ + H_2O \qquad (9)$$

$$CoO^+ + D_2 \rightarrow Co^+ + D_2O \qquad (10)$$

observation of no discernable primary kinetic isotope effect ($k_H/k_D = 1.0$) as obtained from the reaction with D_2 (eq 10).[11a] For comparison, the FeO^+/H_2 couple is more efficient ($k_f = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) with essentially no observable kinetic isotope effect within experimental uncertainty.[11a] Since H—H activation is the only possible pathway for this process, and since no evidence for H atom abstraction has been found, a significant reaction barrier is encountered upon formation of the [CoO^+/H_2] collision complex.

In recent reports, the reaction of FeO^+ with dihydrogen was studied in detail by means of ab initio calculations[5] and experiment.[11a,c] By consideration of ground and excited states of the late-transition-metal oxide cations, a general reaction mechanism was outlined which also applies not only for the reactions of H_2 with the late MO^+ cations but also for the reactions involving hydrocarbons. According to these arguments, the reaction violates spin-conservation rules and involves a curve crossing from the high-spin ground state to a low-spin potential energy hypersurface (Figure 2). This gives rise to a multicentered, energetically low-lying transition structure and results in an entropic bottleneck along the reaction coordinate. Further, the reaction suffers from the short-lived encounter complex caused by the small complexation energy. Preliminary density functional theory calculations on the CoO^+/H_2 system lend further support to the behavior depicted in Figure 2. An analogous scheme was also experimentally established by Armentrout and co-workers for the reaction of CoO^+ with D_2 and CD_4.[31] However, these authors reported that both reactions are very inefficient, and for reaction 10 they determined an upper limit of 0.9×10^{-13} cm^3 molecule^{-1} s^{-1}. With respect to the experimental uncertainties as discussed for the CoO^+/methane system, the background contaminants in particular, we cannot decide yet if reaction 10 does occur at thermal energies, and further experiments are indicated to resolve this dilemma.

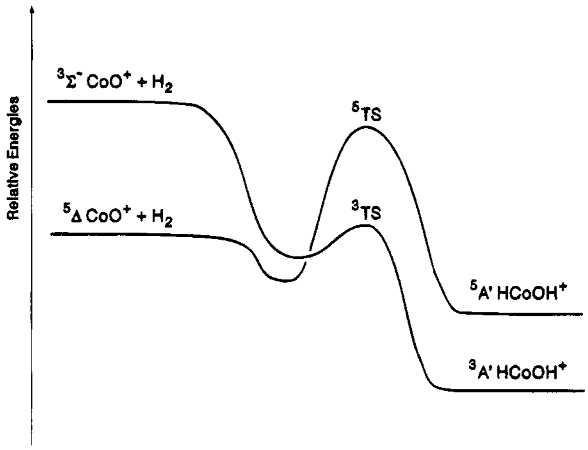

Figure 2. Qualitative potential energy surface for the reaction of H_2 with the $^5\Delta$ and the $^3\Sigma^-$ states of CoO^+. For details, see text and ref 5.

General Trends and Conclusions. Not surprisingly, CoO^+ is more reactive with the larger alkanes relative to small alkanes. This is most evident by the steady increase in the forward rate constants that approach eventually the collisional limit and can be attributed to an increase in polarizability and the lifetime of the excited encounter complexes as one goes from methane to pentane. However, the rate constant for CoO^+/2-methylpropane is two-thirds slower than that for n-butane, although the k_C values are essentially equivalent. One could speculate that the requirements to rearrange the collision complex to the transition states for the product formation may be sterically more congested for i-C_4H_{10}, as was earlier proposed for the Co^+/2-methylpropane couple.[26] Activation of methane by CoO^+, although thermodynamically favorable, is inefficient as compared to that by FeO^+.[8] The interesting yet unsolved question is why is the CoO^+/CH_4 reaction is so slow as compared to FeO^+, although thermochemically the reactions are comparable.

In general, CoO^+ is more reactive than Co^+ toward alkanes and preferentially undergoes initial C—H activation. However, for the larger alkanes the enhanced reactivity is coupled with a decrease of selectivity. For catalytic applications, product distribution control must be demonstrated as an essential feature for the metal complex to be beneficial. From a comparison of the general trends for CrO^+ and more importantly FeO^+, since the latter metal oxide is indeed a gas-phase "catalyst", markedly different reaction patterns can be observed. For CrO^+,[13] also loss of molecular hydrogen is observed in the reactions with propane and higher alkanes. Although the chemistry of FeO^+ is similar to CoO^+ in many regards (thermochemistry and the branching ratios for loss of closed-shell neutral molecules), FeO^+ has a higher propensity to eliminate neutral radicals, whereas neutral organic radical formation for CoO^+ is observed only in the reaction with neopentane. On the other hand, in the reactions with *branched* larger alkanes CoO^+ exhibits properties of a Lewis acid, i.e. it induces methanide transfer. Obviously, work concerning hydrocarbon activation by transition-metal oxides is a potentially rich area of chemistry and further studies to probe the details of these processes are in progress.

Experimental Section

Gas-phase experiments were performed by using a Spectrospin CMS 47X *Fourier*-transform ion-cyclotron resonance mass spectrometer, which is equipped with an external ion source as previously described.[39] Metal ions were generated from laser desorption/ionization by focusing the beam of a Nd: YAG laser (Spectron Systems; $\lambda = 1064$ nm) at a cobalt metal target which was mounted in the external ion source. The Co$^+$ ions were transferred from the external ion source to the analyzer cell by a system of electrostatic potentials and ion lenses. The external ion source, the ion transfer system, and the main vacuum chamber of the spectrometer were differentially pumped by three turbo molecular pumps. The Co$^+$ ions were trapped in the field of a 7 T superconducting magnet (Oxford Instruments). Cobalt ion and the cobalt oxide cation were isolated by using FERETS,[40] a computer-controlled ion ejection protocol which combines single-frequency ion ejection pulses with frequency sweeps to optimize ion isolation. All functions of the instrument, including all pulse sequence steps, were controlled by a Bruker Aspect-3000 minicomputer.

Cobalt oxide was generated from the reaction of N_2O with Co^{+*} (eq 2). Because of the low ion yields, Co$^+$ was allowed to react with pulsed-in N_2O prior to collisional thermalization. Additionally, Co$^+$ was translationally excited by an rf pulse to enhance the production of CoO$^+$. Exact ion masses were evaluated from high-resolution narrow-band 1K spectra (filled to 4K) for all ion excitation pulses. Prior to isolation of CoO$^+$, Ar buffer gas was pulsed in several times, generating ca. 100 thermalizing collisions. Organic reagents were present at static pressures of typically $(1-3) \times 10^{-8}$ mbar, which also served as an additional buffer gas. Pressures were measured by an ion gauge (Lambert) and corrected by using the method previously described by Bartmess and Georgiadis,[41] adjusted to absolute pressure by comparison with ion–molecule reactions of well-established reaction processes.[42] Pseudo-first-order rate constants, reported in this study, were determined from the logarithmic decay of reactant intensity over time and are reported with ±30% error; however, for the slow reactions of hydrogen and methane the error amounts to ±100%.[42] All rate constants were repeated to ensure reproducibility; thus, interferences by nonthermalized ions would be expected to be manifested in ambiguous reaction kinetics. Branching ratios were derived from the analysis of the temporal product distributions and are reported with ±10% error.

Double-resonance experiments[43] performed on suspected reaction intermediates, i.e. $[Co,C_2,H_6,O]^+$ for the reaction of CoO$^+$ with ethane, were performed by first obtaining a high-resolution spectrum (3–5 kHz; 1K data points filled to 4K). The broad-band spectrum was then recorded with rf irradiation at the measured frequency of the intermediate of interest, obtained under high-resolution conditions. Similar procedures were performed for all collisional activation experiments.[44]

[D$_4$]Methane (99 atom % D; MSD), [D$_2$]methane (98% D; Cambridge Isotopes), deuterium (99.5% D; Linde), and $CH_3CD_2CH_3$ (98 atom % D; Cambridge Isotopes) were used as supplied. The labeled compounds CH_3CD_3, $(CH_3)_2CDCH_3$, and $CH_3CH_2CD_2CD_3$ were prepared by hydrolyzing the appropriate Grignard reagents with either H_2O or D_2O as previously reported.[42] Other reagents were obtained in high purity from commerical sources and used as supplied.

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