and Sutton,[8] very low-frequency bending modes of the large chelate rings about the O···O vector (controlled by a single-well potential function) would necessarily require movements of high amplitude on the part of the outer atoms and, therefore, could very well be heavily damped in solution. Such a collisionally damped process is compatible with both the temperature-independent ΔP_0^{VF} values and the previously observed decrease of loss with temperature.[5,7] (Collision damping, while not affecting the polarizations at visible and radio frequencies, would greatly modify the form of the dispersion and absorption curves.[8,9]) In conclusion, although a microwave dispersion of polarization associated with vibrational deformations is rather unusual, this speculation appears to best explain the dielectric behavior when the latter is contemplated in the light of previous observations, notably those from nondielectric studies.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-8121068).

Registry No. Al(acacF$_3$)$_3$, 14354-59-7; Cr(acac)$_3$, 21679-31-2; Fe(acac)$_3$, 14024-18-1; Al(acac)$_3$, 13963-57-0; Co(acac)$_3$, 21679-46-9; H(acac), 123-54-6.

---

(39) J. H. van Vleck and V. F. Weisskopf, *Rev. Mod. Phys.*, **17**, 227 (1945).

(40) N. E. Hill, *Chem. Phys. Lett.*, **2**, 5 (1968).

(41) J. Chamberlain, *Chem. Phys. Lett.*, **2**, 464 (1968).

(42) C. Brot, *Phys. Lett. A*, **30**, 101 (1969).

(43) V. V. Daniel, "Dielectric Relaxation", Academic Press, London and New York, 1957, Chapter 9, pp 130–133.

Gas-Phase Organometallic Chemistry: Chain-Length Effects

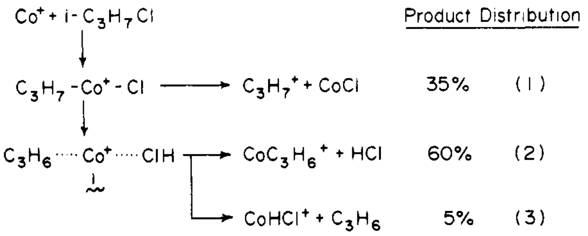
A. Tsarbopoulos and J. Allison*

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. *Received February 20, 1985*

Abstract: The gas-phase chemistry of Co$^+$ with a series of 1-chloro normal alkanes and alcohols with the alkyl chain length varying from three to eight carbon atoms is presented. In the case of chloroalkanes, as the chain length increases, metal ion insertion into internal C–C bonds becomes preferred over that into the C–Cl bond which is the dominant site of insertion for smaller chloroalkanes. The cobalt ion exhibits a much richer chemistry with alcohols by inserting into almost every skeletal C–C bond. A model suggesting metal–carbon atom interactions via cyclic intermediates leading to insertion into C–C bonds at specific distances from the initial site of complexation is used to account for the observed products for alcohols. This may also occur to a lesser extent for the chloroalkanes. The order of preference for the metal insertion is also deduced from these experiments and is contrasted with that of the corresponding alkanes. Trends in the relative probabilities for H shifts from alkyl groups and chloro- and hydroxyalkyl groups are discussed, and H shifts other than β-H shifts are also suggested.

In the past several years a considerable number of studies concerning the chemistry/reactivity of metal and metal-containing ions with organic molecules have appeared in the literature. These studies, performed using ion cyclotron resonance (ICR) spectrometry,[1] Fourier transform mass spectrometry (FTMS),[2] and ion beam techniques[3] have provided thermodynamic, kinetic, and mechanistic information concerning gas-phase organometallic chemistry.

In 1976, Allison and Ridge[4] suggested a metal insertion /β-H shift/competitive ligand loss reaction sequence for explaining the chemistry of gas-phase transition metal ions such as Fe$^+$, Co$^+$, and Ni$^+$ with saturated, monofunctional organic molecules. For example, Co$^+$ (which can be formed by electron impact on Co(CO)$_3$NO) reacts with 2-chloropropane[5] by first inserting into the C–Cl bond. This intermediate can undergo charge transfer and fragment, or a β-H shift can occur, forming two ligands, propene and HCl. Subsequent dissociation of this complex accounts for the major fraction of the observed products.



This mechanism can be used to explain reported reactions such as dehydration of alcohols[5] and dehydrohalogenation of alkyl halides.[5] The mechanism can also be used to explain the chemistry of transition metal ions with most other organic molecules such as ketones[1c,6] and alkanes.[3a,7,8] In the case of small ketones,[1c,6] each R–COR bond is the perferred site of metal insertion, while in the case of alkanes, insertion into C–C bonds and to a lesser extent, C–H bonds, appears to lead to the majority of the products.[7,8]

Based on the chemistry reported to date, one may expect an ion such as Co$^+$ to dehydrate all alcohols. In the case of 1-butanol,[9] this was observed; however, insertion into C–C bonds also occurs. That is, 1-butanol exhibits both "alcohol-like" chemistry and "alkane-like" chemistry. There are other reported cases in which, as the alkyl chain length of a monofunctional organic molecule increases, reactions due to M$^+$ insertion into C–C bonds of the alkyl chain occur in addition to insertion processes "typical" of the functional group. For example, in the chemistry of Fe$^+$ with 2-pentanone, 20% of the products are due to insertion into a C–C bond[1c] (Scheme I). Also, in the case of nitroalkanes,[10] as the alkyl chain length increases, more reactions involving metal insertion into C–C bonds, i.e., away from the polar functional group, are observed.

---

(1) Publications representative of the groups active in this area include: (a) Huang, S. K.; Allison, J. *Organometallics* **1983**, *2*, 883. (b) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794. (c) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Ibid.* **1981**, *103*, 4360. (d) Wronka, J.; Ridge, D. P. *Ibid.* **1984**, *106*, 67.

(2) (a) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, 54, 96. (b) Cody, R. B.; Burnier, R. D.; Cassady, C. J.; Freiser, B. S. *Ibid.* **1982**, *54*, 2225. (c) Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944. (d) Cassady, C. J.; Freiser, B. S. *Ibid.* **1984**, *106*, 6176.

(3) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (b) Armentrout, P. B.; Beauchamp, J. L. *Ibid.* **1981**, *103*, 6628. (c) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (d) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Ibid.* **1983**, *2*, 1818.

(4) Allison, J.; D. B. Ridge *J. Am. Chem. Soc.* **1976**, *98*, 7445.

(5) Allison, J.; D. P. Ridge *J. Am. Chem. Soc.* **1979**, *101*, 4998.

(6) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641.

(7) Halle, L. F.; Houriet, R.; Kappes, M. M.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6293.

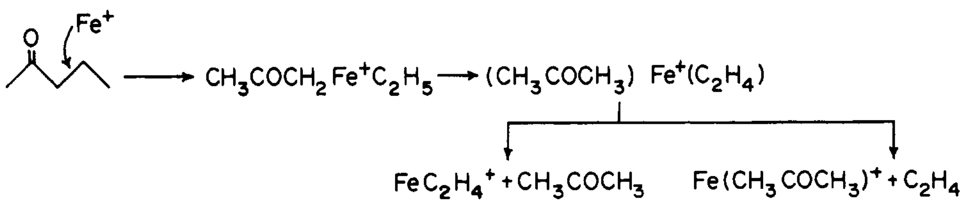
(8) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.

(9) Tsarbopoulos, A.; Allison, J. *Organometallics* **1984**, *3*, 86, 947.

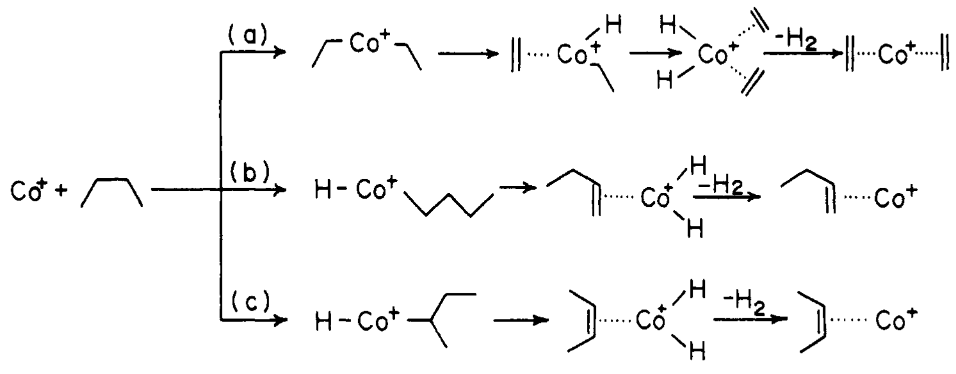
(10) Cassady, C. J.; Freiser, B. S.; McElvany, S. W.; Allison, J. *J. Am. Chem. Soc.* **1984**, *106*, 6125.

0002-7863/85/1507-5085$01.50/0

Scheme I



Scheme II

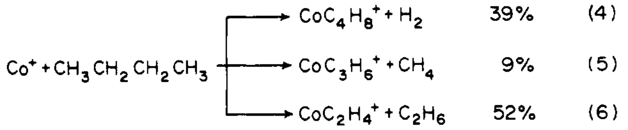


We present here the chemistry of Co^+ with a series of 1-chloro normal alkanes and alcohols. Alkyl chain lengths vary from n-C_3H_7 to n-C_8H_{17}. Our interests are twofold. First, we hope to understand why Co^+ does *not* insert into the C–C bond in ethanol or 2-propanol, but does in 1-butanol; and why, in contrast, Co^+ *only* inserts into the C–Cl bond in ethyl, n-propyl, and n-butyl chlorides. On a larger scale, we are interested in how such chain-length effects could provide insights into the metal-insertion process.

Our long-range goals are to sufficiently understand the three mechanistic steps (metal insertion/β-H shift/competitive ligand loss) such that branching ratios for bimolecular organometallic reactions could be predicted.

To describe our current level of understanding of these mechanistic steps, consider the "simple" case of Co^+ reactions with alkanes.

Metal Ion Insertion Step. Using the suggested mechanism, final reaction products should be indicative of the initial insertion site. For example, if HI elimination from $C_nH_{2n+1}I$ was observed, it would be assumed to occur via insertion into the C–I bond. However, determining which bonds are "attacked" by a metal ion is not always straightforward. Take as an example the chemistry of Co^+ with n-butane.[11]

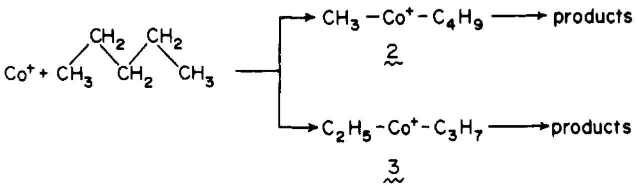


$$Co^+ + CH_3CH_2CH_2CH_3 \rightarrow CoC_4H_8^+ + H_2 \quad 39\% \quad (4)$$
$$\rightarrow CoC_3H_6^+ + CH_4 \quad 9\% \quad (5)$$
$$\rightarrow CoC_2H_4^+ + C_2H_6 \quad 52\% \quad (6)$$

Based on this distribution and the accepted mechanism, we might conclude that Co^+ inserts into the internal C–C bond most often (leading to the products in (6)), with C–H insertion of "second priority" (reaction 4), and insertion into the terminal C–C bond (reaction 5) being least favored. However, this interpretation would not provide a proper description of the chemistry. Beauchamp et al. recently reported that Ni^+ dehydrogenates n-butane exclusively via a 1,4-elimination process.[7] The mechanism suggested involves Ni^+ insertion into the internal C–C bond followed by two β-H shifts, leading to a bis(ethylene) complex with elimination of molecular hydrogen (Scheme IIa). Labeling studies suggest that Co^+ dehydrogenates n-butane by both 1,2- and 1,4-elimination processes (Scheme II).[3d] These studies suggest that Co^+ dehydrogenates butane 51% via Scheme IIa and 49% via Co^+ insertion into C–H bonds, Scheme IIb,c (if the products are interpreted neglecting the possibility of scrambling); however, this distribution may also reflect isotope effects. Jacobson and Freiser[8] suggest that the mechanism in Scheme IIa leads to 90% of the H_2 elimination product, using both CID results and consecutive ligand displacement reactions. Since the Freiser results are free of isotope effects, we will assume that they accurately represent the chemistry.

With this information, i.e., since 90% of the process in reaction 4 follows from the same insertion intermediate involved in reaction 6, the branching ratios would then suggest that 87% of the reaction products in the Co^+-butane system are due to insertion into the internal C–C bond, 9% are due to insertion into the terminal C–C bond, and 4% are due to Co^+ insertion into C–H bonds. Therefore, even for a "simple system", the site of insertion is not always apparent.

Radecki and Allison[11] have interpreted the reaction products for Co^+ with n-alkanes to obtain the order of preference for transition metal ion insertion into skeletal bonds. They point out a correlation between the probability that Co^+ will insert into an R–R′bond and the sum of the ionization potentials (IP) of the corresponding alkyl radicals, $\{IP(R\cdot) + IP(R'\cdot)\}$. Consider, for example, the molecule n-pentane. There are two different skeletal bonds into which metal insertion may occur:



A larger fraction of the products appear to be formed via intermediate **3** than **2**. Also, note that $\{IP(CH_3\cdot) + IP(C_4H_9\cdot)\} > \{IP(C_2H_5\cdot) + IP(C_3H_7\cdot)\}$. It has been proposed that this correlation exists because $IP(R\cdot)$ reflects the polarizability of $(R\cdot)$, and the bond strength $D^\circ(Co^+–R)$ increases as the polarizability of $(R\cdot)$ increases.[3d,11]

Thus, the correlation suggests that, for n-alkanes, the order of preference of Co^+ for insertion into C–C bonds is a consequence of the thermochemistry: when a series of intermediates of the type $R–Co^+–R'$ can be formed, those which are most stable (i.e., those in which the bonds formed are the strongest) are preferred. Note that this holds for a simple case such as the n-alkanes, in which all of the C–C bonds subject to insertion are of (approximately) the same strength.

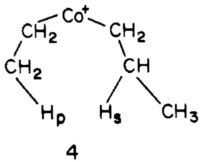
The preference for site of attack vs. $\sum IP(R\cdot)$ correlation provides a useful picture of the metal insertion process for an

---

[11] Radecki, B. D.; Allison, J. *Organometallics*, submitted for publication.

alkane in which many insertion intermediates are formed. The case becomes much more complex for molecules containing a functional group. Available thermodynamic information suggests that Co$^+$ could, in an exothermic process, insert into the C–C or C–OH bonds of ethanol; however, *only* products indicative of the latter are observed. Is the effect of the functional group on the site of insertion a thermodynamic effect, a kinetic effect, or both? This work attempts to answer this question.

β-H Shift Step. While extensive discussions of this particular mechanistic step have not appeared to date, data in the literature can be used to provide insights into the process. An important aspect of the β-H shift is, again, the subject of *preference.* When an intermediate of the type R–Co$^+$–R′ is formed, and both R and R′ contain H atoms which are on carbon atoms that are β to the metal, which will shift to a greater extent (and why)? Take for example, in the case of pentane, intermediate **3**. Two β-H's are accessible:



4

The fact that C_2H_6 elimination is a more prominent process than C_3H_8 elimination (for pentane) suggests that H_s shifts to a greater extent than H_p. Such an analysis of the distribution of products of Co$^+$ with the *n*-alkanes suggests a trend. The β-H shift preferentially occurs from the larger of the two alkyl groups bound to Co$^+$.[3c]

Does the trend still hold when one of the alkyl groups contains a functionality? This question will also be approached in this work.

Competitive Ligand Loss Step. Of the three mechanistic steps, this last step has been characterized most completely. In almost all cases, when the complex M$^+$(A)(B) dissociates, the ligand with the lower proton affinity (PA) is preferentially lost ("PA rule").[9] For example, in the reaction of Fe$^+$ with 2-pentanone,[1c] Scheme I, insertion into a C–C bond leads to the complex $(CH_3COCH_3)Fe^+(C_2H_4)$.

Acetone is the better base in the gas phase, PA(CH_3COCH_3) > PA(C_2H_4), and that is consistent with the observation that retention of acetone is a dominant process. This "PA rule" appears to always hold in the reactions of Co$^+$ with alkanes and all of the reactions presented here.

In this work, we attempt to interpret the products of Co$^+$ with 1-chloro-*n*-alkanes and normal alcohols to suggest an ordering for preferred site of attack of *skeletal* bonds. We will compare these orders of preference with those of the corresponding alkanes to demonstrate the effects due to the functional group. Trends in β-H shifts will also be compared and contrasted.

Experimental Section

All experiments were performed on an ion cyclotron resonance (ICR) spectrometer of conventional design, used in the "drift mode". The instrument was constructed at Michigan State University and is described elsewhere.[12]

The Co$^+$ ions were formed by 70-eV electron impact on $Co(CO)_3NO$. In the experiments which were performed, the chemistry of the $Co(CO)_x^+$ (x = 1, 2) and $Co(CO)_yNO^+$ (y = 0–3) ions was also studied. This work focuses on the chemistry of the bare cobalt cation. To our knowledge, no evidence for the formation of long-lived excited states of Co$^+$ from electron impact on $Co(CO)_3NO$ has appeared. Thus, we cautiously assume that the metal cation is formed in its ground state.

Tricarbonylnitrosylcobalt(0) was obtained from Alfa Inorganics; 1-butanol and 1-chlorooctane were obtained from Alfa Products; 1-chloropentane and 1-chlorohexane were obtained from Fluka Chemical Corp.; 1-hexanol, 1-heptanol, and 1-chloroheptane were obtained from Eastman Kodak Co.; 1-propanol and 1-octanol were obtained from Fischer Scientific Co. The 1-chloropropane was obtained from Aldrich Chemical Co. and the 1-chlorobutane was obtained from Chem-Service, Inc. The 1-pentanol was purchased from J. T. Baker Chemical Co. All samples were degassed by multiple freeze–pump–thaw cycles and were used without further purification.

Table I. Branching Ratios for the Reactions of Co$^+$ with *n*-Propyl, *n*-Butyl, *n*-Pentyl, and *n*-Hexyl X (X = H, Cl, OH)

		X = H[a,b]	Cl	OH
$Co^+ + C_3H_7X$	$\rightarrow C_3H_7^+ + CoX$		0.72	
	$\rightarrow Co(C_3H_6)^+ + HX$	1.00	0.23	0.54
	$\rightarrow Co(HX)^+ + C_3H_6$		0.05	0.14
	$\rightarrow Co(CH_3X)^+ + C_2H_4$			0.09
	$\rightarrow Co(C_2H_3X)^+ + CH_4$			0.02
	$\rightarrow Co(C_3H_7X)^+$			0.21
$Co^+ + C_4H_9X$	$\rightarrow C_4H_9^+ + CoX$		0.81	
	$\rightarrow Co(C_4H_8)^+ + HX$	0.39		
	$\rightarrow Co(HX)^+ + C_4H_8$			0.14
	$\rightarrow Co(C_4H_6)^+ + H_2 + HX$		0.19	0.37
	$\rightarrow Co(C_2H_3X)^+ + C_2H_6$	0.52		0.09
	$\rightarrow Co(C_2H_5X)^+ + C_2H_4$			0.19
	$\rightarrow Co(C_3H_5X)^+ + CH_4$	0.09		
	$\rightarrow Co(C_4H_7X)^+ + H_2$			0.21
$Co^+ + C_5H_{11}X$	$\rightarrow C_3H_7^+ + "CoC_2H_4X"$		0.39	
	$\rightarrow C_5H_{11}^+ + CoX$		0.39	
	$\rightarrow Co(C_5H_{10})^+ + HX$	0.17	0.04	0.08
	$\rightarrow Co(HX)^+ + C_5H_{10}$			0.06
	$\rightarrow Co(C_4H_6)^+ + CH_3X + H_2$		0.07	0.06
	$\rightarrow Co(C_3H_6)^+ + C_2H_5X$	0.57	0.11	0.31
	$\rightarrow Co(C_2H_4)^+ + C_3H_7X$	0.26		
	$\rightarrow Co(C_3H_7X)^+ + C_2H_4$			0.17
	$\rightarrow Co(C_3H_5X)^+ + C_2H_6$			0.07
	$\rightarrow Co(C_4H_7X)^+ + CH_4$			0.04
	$\rightarrow Co(C_5H_9X)^+ + H_2$			0.06
	$\rightarrow Co(C_5H_{11}X)^+$			0.15
$Co^+ + C_6H_{13}X$	$\rightarrow C_3H_7^+ + "CoC_3H_6X"$		0.25	
	$\rightarrow C_4H_9^+ + "CoC_2H_4X"$		0.34	
	$\rightarrow C_6H_{13}^+ + CoX$		0.18	
	$\rightarrow Co(C_6H_{12})^+ + HX$	0.22		
	$\rightarrow Co(HX)^+ + C_6H_{12}$			0.08
	$\rightarrow Co(C_2H_5X)^+ + C_4H_8$			0.10
	$\rightarrow Co(C_4H_8)^+ + C_2H_5X$	0.29	0.11	
	$\rightarrow Co(C_4H_6)^+ + C_2H_5X + H_2$	0.13	0.06	0.11
	$\rightarrow Co(C_3H_6)^+ + C_3H_7X$	0.36	0.06	0.28
	$\rightarrow Co(C_3H_7X)^+ + C_3H_6$			0.13
	$\rightarrow Co(C_4H_7X)^+ + C_2H_6$			0.13
	$\rightarrow Co(C_4H_9X)^+ + C_2H_4$			0.03
	$\rightarrow Co(C_6H_{11}X)^+ + H_2$			0.04
	$\rightarrow Co(C_6H_{13}X)^+$			0.10

[a] H_2 elimination is listed under HX elimination for X = H. [b] Reference 11.

In a typical experiment, low- and high-pressure spectra of each compound were taken, and any ion/molecule reactions due to the organic system alone were identified and their precursors were determined by ion cyclotron double resonance. Then ion/molecule reaction products (up to *m/z* 270) were identified and their precursors were determined by double resonance techniques in 1:1 or 1:2 (by pressure) mixtures of $Co(CO)_3NO$/organic at total pressures up to 1.0×10^{-5} torr. The results of these experiments are listed in Tables I and II. The observed reactions are facile and dominant reactions have rate constants within an order of magnitude of the collision frequency. In the case of 1-butanol, instrumental improvements have enabled us to accurately determine the contribution of each precursor for the previously observed[9] minor product ions at *m/z* 103, 105; the branching ratios for the products of Co$^+$ and 1-butanol reflect these new results.

Ion/molecule reaction product identification was straightforward except in the case of 1-octanol. One product at *m/z* 127 remains unidentified in Table II. It is a reaction product of Co$^+$ and could be $CoC_4H_4O^+$, $CoC_5H_8^+$, or $C_8H_{15}O^+$.

Results and Discussion

β-H Shifts. While the main purpose of this study is to provide information concerning the metal-insertion process, some interesting insights into the β-H shift process can also be derived. Since the implications of the β-H shift trends are pertinent to the data interpretation which follows, we present them first.

The particular aspect of the β-H shift which we address here concerns intermediates of the type

$$R\text{–}Co^+\text{–}R'$$

where both R and R′ have β-H atoms that can shift. Halle, Armentrout, and Beauchamp[3c] first pointed out, in the case of intermediate 4, that the shift of a secondary β-H is preferred over

---

(12) Radecki, B. D.; Allison, J. *J. Am. Chem. Soc.* **1984**, *106*, 946.

Table II. Branching Ratios for the Reactions of Co$^+$ with *n*-Heptyl and *n*-Octyl X (X = H, Cl, OH)

		X = H^{a,b}	Cl	OH
Co$^+$ + $C_7H_{15}X$	$C_4H_9^+$ + "CoC_3H_6X"		0.41	
	$C_5H_9^+$ + {CoX + C_2H_6}		0.07	
	$C_7H_{15}^+$ + CoX		0.18	
	$Co(C_7H_{14})^+$ + HX	0.12		
	$Co(C_5H_{10})^+$ + C_2H_5X	0.10	0.19	
	$Co(C_2H_5X)^+$ + C_5H_{10}			0.03
	$Co(C_4H_8)^+$ + C_3H_7X	0.51		0.24
	$Co(C_3H_7X)^+$ + C_4H_8			0.07
	$Co(C_3H_5X)^+$ + C_4H_{10}			0.04
	$Co(C_4H_6)^+$ + H_2 + C_3H_7X		0.06	0.14
	$Co(C_3H_6)^+$ + C_4H_9X	0.27	0.09	0.14
	$Co(C_4H_9X)^+$ + C_3H_6			0.01
	$Co(C_4H_7X)^+$ + C_3H_8			0.12
	$Co(C_7H_{15}X)^+$			0.21
Co$^+$ + $C_8H_{17}X$	$C_5H_9^+$ + {CoX + C_3H_8}		0.10	
	$Co(C_8H_{16})^+$ + HX	0.05	0.10	
	$Co(C_6H_{12})^+$ + C_2H_5X	0.09	0.45	0.05
	$Co(C_5H_{10})^+$ + C_3H_7X	0.18	0.17	0.11
	$Co(C_3H_7X)^+$ + C_5H_{10}			0.06
	$Co(C_4H_8)^+$ + C_4H_9X	0.29		0.08
	$Co(C_4H_9X)^+$ + C_4H_8			0.02
	$Co(C_4H_7X)^+$ + C_4H_{10}			0.18
	$Co(C_4H_6)^+$ + H_2 + C_4H_9X			0.04
	$Co(C_3H_6)^+$ + $C_5H_{11}X$	0.39	0.18	0.22
	$Co(C_5H_{11}X)^+$ + C_3H_6			0.01
	$Co(C_8H_{15}X)^+$ + H_2			0.05
	$Co(C_8H_{17}X)^+$			0.09
	(m/z 127)			0.09)

[a] H_2 elimination is listed under HX elimination for X = H. [b] Reference 11.

that of a primary β-H; thus, more $CoC_3H_6^+$ results from **4** than $CoC_2H_4^+$. This is also the case for the Fe$^+$ and Ni$^+$ analogues of **4**.

A similar analysis of the data in Tables I and II for alkanes expands on this concept. In the case of pentane we see that a β-H shift from an *n*-propyl group is favored over that from an ethyl group. We will use the shorthand notation β-H (n-C_3) > β-H (C_2). In the case of hexane, some products are formed through the intermediate

$$C_2H_5-Co^+-C_4H_9$$

In this case, the β-H shift from the *n*-C_4H_9 group dominates. In fact, *no* products from the primary β-H shift are observed. The reaction products for Co$^+$ with heptane suggest that β-H (n-C_5) > β-H (C_2) and β-H (n-C_4) > β-H (n-C_3). Results for octane suggest that β-H (n-C_6) > β-H (n-C_2), but suggest a reversal of the trend in that β-H (n-C_3) > β-H (n-C_5). Beauchamp's results for Co$^+$ and octane show the expected order,[7] with the β-H (C_5) shift being slightly favored over the β-H (C_3) shift.

The results of Radecki and Allison[11] for nonane and decane also suggest that the probability for β-H shift from *n*-C_nH_{2n+1} is not a simple function, monotonically increasing with increasing *n*. Products from the reaction of Co$^+$ and nonane suggest that β-H (n-C_3) > β-H (n-C_6) and β-H (n-C_4) > β-H (n-C_5). The decane results suggest that β-H (n-C_8) > β-H (C_2), β-H (n-C_7) > β-H (n-C_3) and β-H (n-C_4) > β-H (n-C_6).

Thus, the chemistry of Co$^+$ with alkanes suggests that, when two alkyl groups are present in a metal-insertion intermediate which both contain β-H's, the probability that a β-H shift will result from a particular alkyl group follows the order:

$$\beta\text{-H}(C_2H_5) < \beta\text{-H}(n\text{-}C_3H_7) < \beta\text{-H}(n\text{-}C_4H_9)$$

However, it is unclear how the larger alkyl groups fit into this ordering.

Does this trend also hold in the reactions of the chloroalkanes? That is, is the probability of a β-H shift from $-CH_2CH_2Cl$ the same as that for $-CH_2CH_3$? Consider as an example, the products for *n*-chlorooctane resulting from the intermediate

$$C_3H_7-Co^+-(CH_2)_5Cl$$

The results in Table II suggest that only the β-H from the *n*-C_3H_7 group shifts. In fact, an analysis of the chloroalkane results in Tables I and II reveals that a β-H shift from a chloroalkyl group *never* occurs. We conclude that this is a kinetic effect. A subsequent metal–halogen interaction following Co$^+$ insertion into various C–C bonds

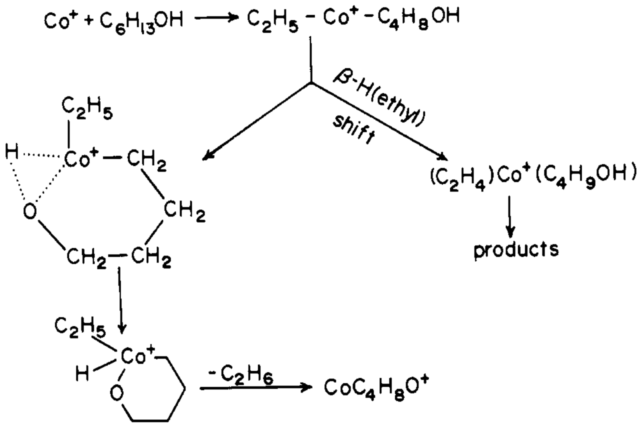
moves the β-H atoms of the chloroalkyl group away from the metal making them inaccessible. This explanation has been used previously to explain the failure of a β-H shift to occur.[10]

We would assume that a similar M–O interaction would lead to the same trend for alcohols. In the case of pentanol, the intermediate

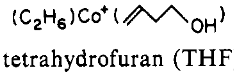
$$C_3H_7-Co^+-C_2H_4OH$$

is apparently formed. *No* products resulting from a β-H shift from the hydroxyethyl group are observed. There are instances where H shifts from $-(CH_2)_2OH$ in (butanol) and $-(CH_2)_3OH$ (in butanol and heptanol) are observed, but a β-H shift from the alkyl group is always preferred. There is *one* hydroxyalkyl group for which a H shift consistently occurs preferentially over whatever alkyl group is present; this is the $-(CH_2)_4OH$ group. We suggest that, in this case, a six-membered ring intermediate is formed in which a significant Co$^+$–O interaction weakens the O–H bond, facilitating the H shift as shown in Scheme III for hexanol.

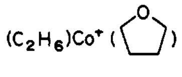
Scheme III



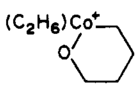
That is, we suggest that it is not a β-H shift which occurs from a $-(CH_2)_4OH$ group, but an ϵ-H shift. This is consistent with the observation that a H shift from $-(CH_2)_4Cl$ is not observed. Since it is not a β-H shift, the intermediate formed in Scheme III is probably not



but contains either tetrahydrofuran (THF)



or a metallacycle:



This observation also provides some interesting insights into the H_2 elimination reactions. We indicated earlier that, at least in the case of Co$^+$ reacting with *n*-butane, almost all of the H_2 elimination reaction is due to Co$^+$ insertion into the internal C–C bond followed by β-H shifts from both alkyl groups. We note that reactions in which only H_2 is eliminated are not observed for the chloroalkanes in Tables I and II. Following Co$^+$ insertion into C–C bonds, H atoms from chloroalkyl groups do not shift onto the metal; this reinforces the concept of H_2 elimination being

Scheme IV

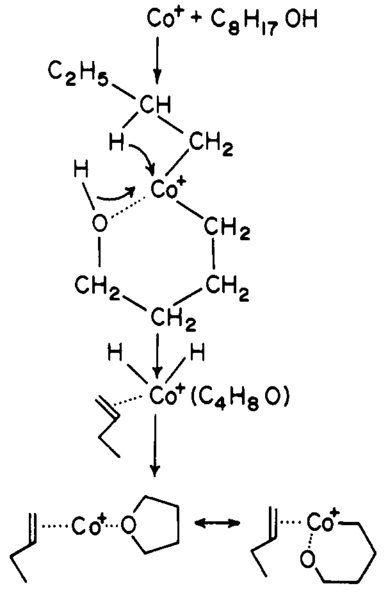
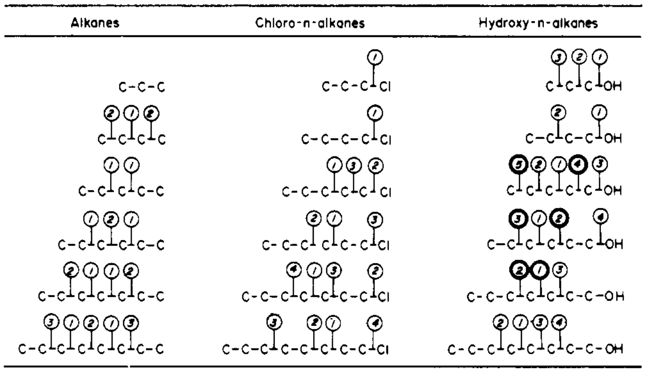


Table III



Alkanes	Chloro-n-alkanes	Hydroxy-n-alkanes
C-C-C	C-C-C①Cl	C③C②C①OH
C②C①C②C	C-C-C-C①Cl	C-C②C-C①OH
C-C①C①C-C	C-C-C①C③C②Cl	C⑤C②C①C④C③OH
C-C①C②C①C-C	C-C-C②C①C-C③Cl	C-C③C①C②C-C④OH
C-C②C①C①C②C-C	C-C-C④C①C③C-C②Cl	C-C-C②C①C③C-C-OH
C-C③C①C②C①C③C-C	C-C-C③C-C②C①C-C④Cl	C-C-C②C①C③C④C-C-OH

[a] The ordering of bond insertion preference for alcohols shown here assumes that the $Co(C_4H_6)^+$ product is formed by H_2 loss from $Co(C_4H_8)^+$. If $Co(C_4H_6)^+$ is formed by dehydration of $Co(C_4H_8O)^+$, the numbers in the *double circles* will switch.

predominantly the result of metal insertion into C–C, *not* C–H bonds. We note that Co^+-induced H_2 elimination is observed for some of the alcohols. Since the hydrogen atom which shifts from hydroxyalkyl groups appears to be the hydroxy hydrogen atom, and most likely from the $-(CH_2)_4OH$ group, H_2 elimination for alcohols must be predominantly a 1,7 elimination. Using 1-octanol as an example, Scheme IV shows the H_2 elimination following insertion into the C_4H_9–C_4H_8OH bond.

Similarly we suggest that H_2 elimination from 1-hexanol predominantly follows Co^+ insertion into the C_2H_5–C_4H_8OH bond. Since H_2 elimination is neither a 1,2 nor a 1,4 elimination for these alcohols, it is not observed for propanol.

Order of Preference for the Metal Insertion: Considerations Leading to Table III. The alkane chemistry suggests an ordering of preference for site of attack of skeletal C–C bonds by Co^+. The reasoning leading to the information in Table III follows the discussion of alkane chemistry in the Introduction, and has been discussed by Radecki and Allison.[11] In Table III, a bond labeled ① is that bond into which Co^+ insertion occurs most frequently, i.e., is most "preferred". Insertion into this bond leads to the largest fraction of the products. The bond into which Co^+ insertion leads to the next largest fraction of the products is labeled ②, etc. If no products due to insertion into a bond are detected, it is not given an "order of preference" rating.

We note that a number of other reports of the reaction products of Co^+ with *n*-alkanes have appeared. While actual values for branching ratios vary from lab to lab, all results suggest the "order of preferences" shown in Table III (except for propane). A comparison of the various works on alkanes is given in footnote 11.

When interpreting results to produce an ordering for site of insertion, a decision must be made concerning products which could be formed by more than one mechanism. Also, in light of the 1,4-dehydrogenation process reported for alkanes, H_2 elimination is always difficult to deal with. Fortunately, in the reactions reported, H_2 elimination is frequently a minor process, such that it does not affect the overall ordering if it does occur via Co^+ insertion into skeletal bonds (as opposed to insertion into C–H bonds). To indicate typical problems which arise in an attempt to determine the information for the polar compounds in Table III, consider the case of 1-heptanol. There are six C–C bonds and one C–OH bond into which Co^+ may insert:

$$C^7-C^6-C^5-C^4-C^3-C^2-C^1-OH$$

The relationship between many products and site of attack is apparent. Insertion into the C^2–C^3 bond leads to the product $CoC_2H_5OH^+$. This appears to be a minor process. Metal insertion into the C^1–C^2 bond does not appear to occur. It is not apparent how the $CoC_4H_6^+$ ion is produced. If $CoC_4H_8^+$ loses H_2 to form $CoC_4H_6^+$, then the $CoC_4H_6^+$ ion follows insertion into the C^3–C^4 bond. If $CoC_4H_6^+$ is a dehydration product of $Co(C_4H_8O)^+$, then the ion is formed owing to insertion into the C^4–C^5 bond. In the β-H shift discussion we mention three forms of $CoC_4H_8O^+$, where the ligand may be THF, the "metallacycle of THF", or 3-buten-1-ol. It has been reported that, when Co^+ reacts with 3-buten-1-ol, $CoC_4H_6^+$ constitutes 80% of the products;[9] 26% of the reaction products of Co^+ with THF are $CoC_4H_6^+$.[12] Thus, the process

$$CoC_4H_8O^+ \longrightarrow CoC_4H_6^+ + H_2O$$

is possible. Also, Co^+ reacts with $1-C_4H_8$ to form $CoC_4H_6^+$, which is the major reaction product (97%).[13] Since $CoC_4H_6^+$ is formed in the chloroalkanes, and based on the β-H shift discussion, the trends in Table III are based on the assumption that $CoC_4H_8^+$ leads to $CoC_4H_6^+$, i.e., is reflective of insertion into the C^3–C^4 bond of 1-heptanol. Thus, insertion into the C^3–C^4 bond leads to the products $CoC_4H_8^+$, $CoC_4H_6^+$, $CoC_3H_7OH^+$, and $CoC_3H_5OH^+$, which represents 47% of the products observed; 25% of the products, $CoC_3H_6^+$, $CoC_4H_9OH^+$, and $CoC_4H_7OH^+$ follow Co^+ insertion into the C^4–C^5 bond.

Therefore, the ordering of preferences for site of attack of skeletal bonds by Co^+ is:

$$C^3-C^4 > C^4-C^5 > C^1-OH > C^2-C^3$$

If the $CoC_4H_6^+$ ion has as its precursor $CoC_4H_8O^+$, the ordering changes to:

$$C^4-C^5 > C^3-C^4 > C^1-OH > C^2-C^3$$

Note that only the order between two adjacent skeletal bonds has been changed. A similar situation exists for the other alcohols as well. The analogous situation does not exist for the chloroalkanes, since no $CoC_4H_7Cl^+$ ion is observed (which could lose HCl to form $CoC_4H_6^+$).

Thus based on an analysis of the products in Tables I and II, using previous results and the specific processes suggested in the β-H shift discussion, the orders of preference for site of insertion into skeletal bonds by Co^+ are presented in Table III.

Chemistry of Co^+ with 1-Chloro-*n*-alkanes. Reactions 1–3 are typical for small alkyl halides. The results for 1-chloropropane in Table I are typical in that Co^+ reacts by Cl^- abstraction and by the metal–insertion/β-H shift mechanism, following insertion into the C–Cl bond. The process

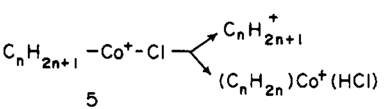
$$RX + Co^+ \longrightarrow R^+ + CoX \quad (7)$$

is observed only for the chloroalkanes in Tables I and II. In the

---

[13] Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624.

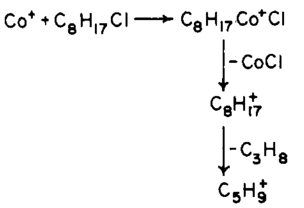
case of R = C_3H_7, reaction 7 is exothermic only for X = Cl. This is a result of the facts that C–Cl bonds are weaker than C–C, C–OH, and C–H bonds,[14] and the Co^0–Cl[16] bond is stronger than the Co^0–CH_3[15] and Co^0–H[15] bonds, and possibly the Co^0–OH[16] bond. *If* the exothermic chloride abstraction process occurs following Co^+ insertion into the C–Cl bond, we have two processes competing: charge transfer and the β-H shift:



5

Tables I and II show that, as n increases, intermediate **5** tends to dissociate to $C_nH_{2n+1}{}^+$, rather than undergo the β-H shift. This is expected since the alkyl ion formation becomes *increasingly* exothermic, since IP(C_nH_{2n+1}) decreases with increasing n. Because of this, $Co(HCl)^+$ and $Co(C_nH_{2n})^+$ products are not observed for the larger chloroalkanes in Tables I and II.

While, we expect reaction 7 to become increasingly favored for larger chloroalkanes, we note that we do not observe the $C_8H_{17}{}^+$ cation in the case of chlorooctane. We do observe $C_5H_9{}^+$ as a product ion. We know from the electron impact mass spectra of n–alkanes that large alkyl cations are relatively unstable. After considering a number of low-energy decomposition pathways of $C_8H_{17}{}^+$ (via loss of C_nH_{2n} and C_nH_{2n+2} neutrals), we note that one of *the* lowest energy decompositions corresponds to loss of propane to form $C_5H_9{}^+$, possibly c-$C_5H_9{}^+$.[17] Thus, failure to observe $C_8H_{17}{}^+$ may be due to rapid fragmentation following its formation:



We note that, in the chemistry of $C_nH_{2n+1}Cl$, Co^+ inserts into other (i.e., C–C) skeletal bonds instead of exclusively into the C–Cl bond when $n \geq 4$. That is, "alkane-like" chemistry is observed in addition to "alkyl halide-like" chemistry. When Co^+ inserts into a C–C bond, a β-H shift leads to the intermediate (alkene)-Co^+(chloroalkane). Since chloroalkanes have lower PA's than alkenes, the chloroalkane is preferentially lost in every case.

Table IV. Bond Dissociation Energies (kcal/mol)[a]

Bond	Energy	Bond	Energy
$CH_3CH_2CH_2$-CH_3	85	$CH_3CH_2CH_2CH_2$-CH_2OH	85[b]
$CH_3CH_2CH_2CH_2$-CH_3	85	$CH_3CH_2CH_2CH_2$-CH_2Cl	86[b]
$CH_3CH_2CH_2$-CH_2CH_3	82	$CH_3CH_2CH_2$-CH_2CH_2Cl	82[b]
CH_3CH_2-$CH_2CH_2CH_3$	82	CH_3CH_2-$CH_2CH_2CH_2Cl$	82[b]
CH_3-CH_3	88	CH_3-$CH_2CH_2CH_2CH_2Cl$	85[b]
CH_3-CH_2OH	83		
CH_3-CH_2Cl	88		

[a] Values taken from ref 20–22. [b] Calculated by using the group equivalence data in ref 21.

In the chemistry of the larger $C_nH_{2n+1}Cl$ molecules, smaller alkyl cations ($C_mH_{2m+1}{}^+$; $m < n$) are formed, apparently following Co^+ insertion into C–C bonds. These processes parallel reaction 7. For intermediates of the type

$$C_mH_{2m+1}\text{-}Co^+\text{-}C_fH_{2f}Cl$$

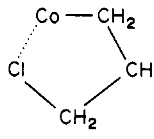
as m increases, formation of $C_mH_{2m+1}{}^+$ is favored over the β-H shift/competitive ligand loss sequence. In this way $C_3H_7{}^+$ is formed from 1-chloro-n-pentane and 1-chloro-n-hexane; $C_4H_9{}^+$ is formed from 1-chloro-n-hexane and 1-chloro-n-heptane, etc. Similar products are reported in *endothermic* reactions of Co^+ with alkanes.[3a] Again, the presence of the Cl group makes this process exothermic for the larger R–X, only where X = Cl. Consider the reaction

$$Co^+ + n\text{-}C_7H_{15}Cl \longrightarrow C_4H_9^+ + \text{"}CoC_3H_6Cl\text{"} \quad (8)$$

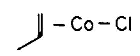
The possible neutral products may be:

$CoCl + C_3H_6$

6



7



8

The reported products cannot be CoCl and propene, **6**, since the overall reaction would be endothermic by approximately 12 kcal/mol. Since $D°(Co^0–CH_3) = 41 \pm 10$ kcal/mol[15] and $D°(Co^0–Cl) = 92.8 \pm 1.9$ kcal/mol,[16] we prefer structure **8** over **7**. Reaction 8 would be exothermic if the metal product was **8**, and if $D°(ClCo^0–C_3H_6) > 10.8$ kcal/mol, which would not be unlikely. If the Co–Cl interaction in intermediate **7** was sufficient to make (8) exothermic, we would also expect to observe the analogous reaction for 1-heptanol. Since we do not observe this, and since D(R-Cl) < D(R-OH),[14] we suggest that reaction 8 occurs via Co^+ insertion into the C_4H_9–C_3H_6Cl bond, and, as charge transfer occurs to form $C_4H_9{}^+$, the CoC_3H_6Cl, **7**, rearranges to **8**, prior to fragmentation.

In light of this discussion, we note that the reaction

$$Co^+ + n\text{-}C_7H_{15}Cl \longrightarrow C_5H_9^+ + \{CoCl + C_2H_6\}$$

is approximately 20 kcal exothermic if the neutral products are CoCl and C_2H_6. Thus, rather than considering $C_5H_9{}^+$ as ($C_5H_{11}{}^+$ – H_2), we will assume it is formed via Co^+ insertion into the C–Cl bond followed by charge transfer to form $C_7H_{15}{}^+$ which subsequently loses C_2H_6.

The branching ratios in Tables I and II lead to the preference for site of attack orderings for the chloroalkanes in Table III. A number of trends can be noted.

First, Co^+ is selective *against* insertion into terminal C–C bonds (both in the alkanes and chloroalkanes). This is, in part, due to the fact that these bonds are stronger than the internal C–C bonds by approximately 3 kcal/mol (Table IV). The C–CH_2Cl bond (the *other* terminal C–C bond) also remains intact, except in the case of n-pentyl chloride, a situation in which the unusually stable cobalt–butadiene complex is formed.[18] This bond is also approximately 4 kcal/mol stronger than the internal C–C bonds (Table IV).

Second, as the chain length of the alkyl chloride increases, metal ion insertion into internal C–C bonds becomes preferred over insertion into the C–Cl bond, which is the dominant site of insertion for the smaller chloroalkanes.

Third, there are a number of similarities between the preferred site of attack orderings for the chloroalkanes and their alkane analogues. For example, in both chlorohexane and hexane, Co^+

---

[14] In n-C_3H_7X (X = OH, Cl) the bond strengths of the C^3–C^2, C^2–C^1, C–H, C^1–OH, and C^1–Cl bonds are 85, 86, 98, 91, and 81 kcal/mol, respectively.[21]

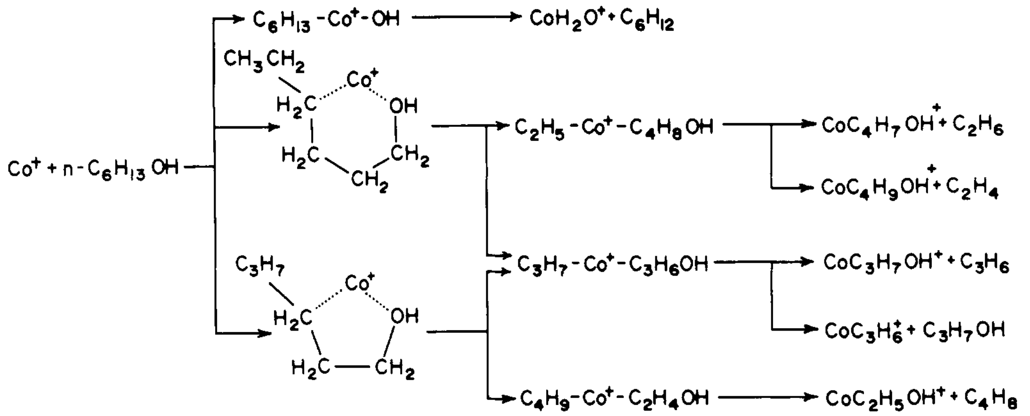
[15] $D(Co^0–H) = 39 \pm 6$ kcal/mol, $D(Co^0–CH_3) = 41 \pm 10$ kcal/mol from ref 3a.

[16] Since Co^+ reacts with 2-propanol by hydroxide abstraction leading to formation of the 2-propyl cation, a lower limit can be deduced, $\Delta H_f°$-(CoOH) < 27.4 kcal/mol. Using this value we can place a lower limit on the cobalt-hydroxy bond strength, $D(Co^0–OH) \geq 83.4$ kcal/mol. Since Co^+ does not form n-$C_3H_7{}^+$ from 1-propanol (Table I), an upper bound is suggested, $D(Co^0–OH) < 99.1$ kcal/mol. From the value of $\Delta H_f°(CoCl) = 37.81 \pm 1.87$ kcal/mol, we can also estimate the cobalt–chloride bond strength, $D(Co^0–Cl) = 92.8 \pm 1.9$ kcal/mol: Kulkarni, M. P.; Dadape, V. V. *High Temp. Sci.* **1971**, *3*, 277.

[17] For example, the loss of propane is approximately 18 kcal/mol more exothermic than the loss of ethane.[21]

[18] Studies of the chemistry of Co^+ with olefins have suggested 45–60 kcal/mol as the estimate for the bond strength between Co^+ and 1,3-alkadienes.[13] A lower limit on the cobalt-butadiene bond strength, $D(Co^+–C_4H_6) > 43.3$ kcal/mol, has been also reported.[9]

Scheme V



most often inserts into the C^2–C^3 bond, leading to products containing four and two carbon atoms. This may be related to the observation that, as the chain length increases, the most preferred site of attack moves away from the functional group. It appears that a propyl group always remains intact at the end of each chain. This is presumably related to the concept that the most preferred insertion intermediates are those which are the more stable, and the most stable intermediates are formed (in the case of alkanes) when the strongest Co$^+$–C$_n$H$_{2n+1}$ bonds are formed, which increase with increasing n.[19]

Fourth, while the chloroalkane order of preference for site of insertion has much in common with those for the alkanes, the match is not exact. That is, the reaction products for e.g., chlorohexane, are not the sum of the reaction products for hexane (with the Cl not participating) plus products following insertion into the C–Cl bond.

Chemistry of Co$^+$ with 1-Hydroxy-*n*-alkanes. The metal insertion/β-H shift/competitive ligand loss sequence can be used to explain the Co$^+$-induced dehydration reaction of alcohols, which is the major process observed for small alcohols such ethanol. In the case of 1-propanol (Table I), Co$^+$ insertion into the C–OH bond accounts for only 70% of the products. Insertion into the C–C bonds leading to C$_2$H$_4$ and CH$_4$ elimination also occurs; these "alkane-like" reactions were not observed for either ethanol or 2-propanol. Ethylene elimination from 1-propanol occurs through intermediate **9**. This is consistent with the relative proton affinities

$$Co^+ + n\text{-}C_3H_7OH \longrightarrow \underset{\mathbf{9}}{(C_2H_4)Co^+(CH_3OH)} \longrightarrow CoCH_3OH^+ + C_2H_4$$

(PA(CH$_3$OH) > PA(C$_2$H$_4$)) which would suggest that C$_2$H$_4$ loss should be dominant.

The number of reaction products for alcohols rapidly increases with increasing alkyl chain length. Co$^+$ insertion into almost every skeletal C–C bond occurs, with the exception of the C–C bond which is α with respect to the functional group. This bond is approximately 3 kcal/mol stronger than the other skeletal bonds owing to the presence of the OH group (Table IV). An exception is in the case of pentanol, where insertion into this C–C bond leads to the very stable CoC$_4$H$_6^+$.

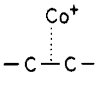
For the larger alcohols, we report CoH$_2$O$^+$ as a product, but no corresponding Co(olefin)$^+$. The larger olefins should have proton affinities greater than that of H$_2$O, and thus Co(olefin)$^+$ products should be observed. Since alcohols are hydrophilic, the presence of trace amounts of H$_2$O present cannot be ruled out, although it could not be detected. Thus, we cannot be certain that the small CoH$_2$O$^+$ products are indicative of Co$^+$ insertion into the C–OH bond. Fortunately, in all cases where the corresponding Co$^+$(olefin) product is not observed, the CoH$_2$O$^+$ ions are minor products.

A number of observations concerning the ordering of preferred site of attack for the alcohols (Table III) warrant discussion.

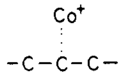
First, as the alkyl chain length increases, insertion into the C–OH bond becomes a minor pathway and attack of C–C bonds dominates. In fact, if the CoH$_2$O$^+$ ions are due to trace amounts of water, then insertion into C–OH does not occur at all for the larger alcohols.

Second, as the alkyl chain gets larger, attack of C–C bonds farther from the OH occurs *only up to a certain point.* For example, all the bonds including the terminal C–C bond of pentanol are attacked by Co$^+$. The terminal bond of hexanol is *not* attacked. The *two* C–C bonds farthest from the functional group in heptanol are not attacked.

Third, the bonds numbered ① and ②, i.e., those most susceptible to attack, are always *adjacent* in the alcohols. This prompted the consideration of how Co$^+$ inserts into a C–C bond. One may consider the process to occur either through an initial interaction of Co$^+$ with the bonding electrons of a C–C bond, **10**, or by initial interaction of Co$^+$ with a C atom, **11**. We assume

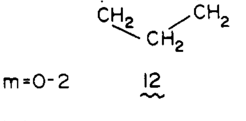


10

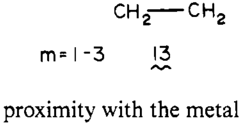


11

the latter, **11**. For small molecules such as ethanol, Co$^+$ initially complexes with a lone pair on the hydroxy group. This interaction weakens the C–OH bond making it susceptible for attack. If Co$^+$ interacts with a skeletal C atom, the bonds to that C atom become weakened and thus susceptible to attack. Thus if Co$^+$ preferentially interacts with one particular C atom in the chain, we might expect that the two C–C bonds containing this C would be most likely attacked, and thus exhibit a high preference. We suggest that, owing to the relatively high PA of alcohols, Co$^+$ first complexes with the OH group in all of the alcohols. Following this, a five- or six-membered ring intermediate (**12**, **13**) can be formed,



m=0-2 **12**



m=1-3 **13**

bringing specific skeletal atoms into close proximity with the metal ion. These Co$^+$–C interactions weaken the adjacent C–C bonds making them susceptible to insertion.

---

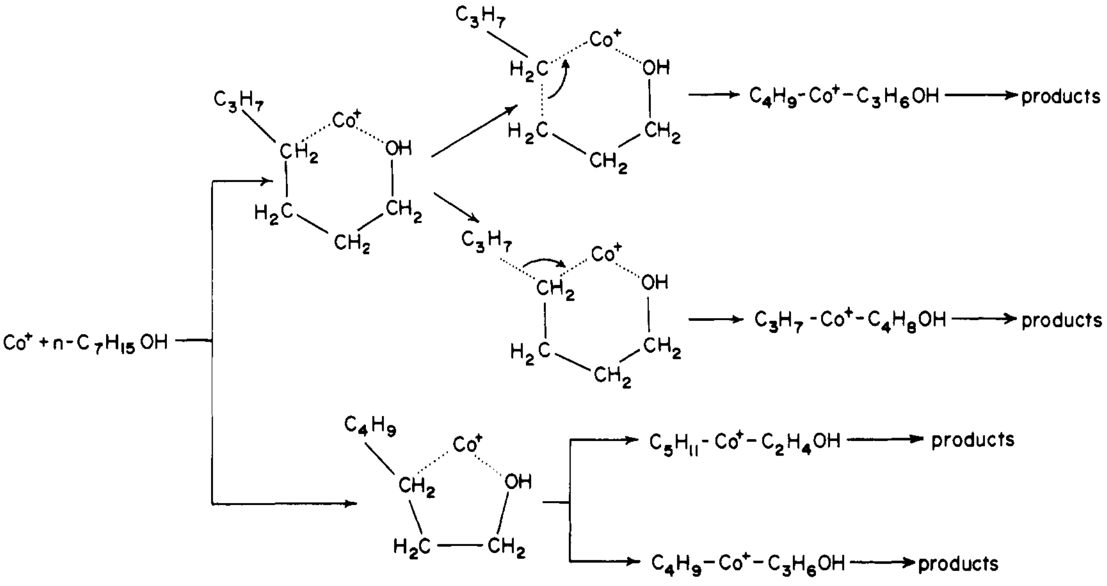
(19) For alkyl groups (C$_n$H$_{2n+1}$), as n increases, the polarizability increases, leading to a larger $D°$(Co$^+$–C$_n$H$_{2n+1}$).[11]

(20) West, R. C., Ed. "Handbook of Chemistry and Physics", 57th ed.; CRC Press: Cleveland, 1977.

(21) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. *Natl. Stand. Ref. Data Ser., Natl. Bureau Std.* **1969**, *26* (NSRDS-NBS26).

(22) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, 6.

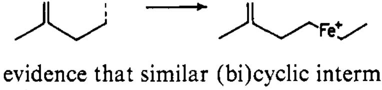
Scheme VI



The formation of the five- and six-membered ring intermediates along with all of the possible insertion intermediates and the resulting products are shown in Scheme V for 1-hexanol. Using this model, which first became apparent in the case of 1-pentanol, all of the major products can be predicted for the longer chain ($n \geq 6$) alcohols. Scheme VI uses the concept to show that it can be used to account for all of the major products of 1-heptanol. The reactions of octanol could be explained in this way, allowing a seven-membered ring intermediate to form as well on complexation.

Thus, we propose that for alcohols a Co^+(HOR) complex is formed initially. The initial Co^+–O interaction weakens the C–OH bond making it susceptible to attack. Through cyclic intermediates, C atoms (C^3, C^4) in the alkyl group come into close proximity to Co^+. The resulting CH_2–Co^+ interactions weaken specific C–C bonds, which become spatially accessible for attack by Co^+. We assume that the most stable insertion products are formed. In the case of butanol, insertion into the C–OH bond gives the most stable intermediate, while in the larger alcohols, products of the type R''–Co^+–$R'OH$ appear to be more stable than the R–Co^+–OH intermediate. Note that, using these cyclic intermediates to make C–C bonds spatially accessible to Co^+ for insertion, the C^1–C_2 bond should not be attacked.

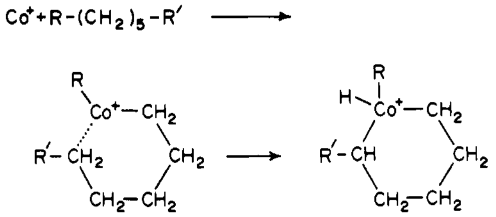
The suggested scheme invoking metal–C interactions through cyclic intermediates leading to insertion into C–C bonds at specific distances from the initial site of complexation can also be used to explain some of the results in the literature. For example, Fe^+ reacts with small ketones by inserting into the various C–CO bonds.[1c] However, when the alkyl chain length increases, specific C–C bonds are attacked. For example, Fe^+ eliminates C_2H_4 from 2-hexanone. Attack of the C–C could be explained via a cyclic intermediate.



There is also evidence that similar (bi)cyclic intermediates dominate the site of attack preference in the chemistry of Co^+ with bifunctional molecules of the type $Cl(CH_2)_5X$, X = Br, OH.[23]

In light of the utility of mechanisms involving cyclic intermediates leading to insertion into C–C bonds, analogous mechanisms may lead to insertion into C–H bonds. That is, if a metal ion complexes with a functional group and a C in the attached alkyl chain interacts with the metal through a cyclic intermediate, *all* bonds to that C may be weakened and thus susceptible to metal insertion, including C–H bonds. In fact, Freiser et al.[1c] suggested such mechanisms to explain H_2 elimination reactions in the chemistry of Fe^+ with labeled ketones, in which Fe^+ complexes with the carbonyl oxygen and inserts into C–H bonds via five- and six-membered ring intermediates.

We also suggested H shifts via cyclic intermediates following Co^+ insertion into a bond, such as in the case of R–Co^+–$(CH_2)_4$–OH. We suggest that similar behavior occurs with sufficiently long alkyl groups as well. This prompts a second look at the β-H shift data for alkanes. We note that the β-H shift trend for alkyl groups appears to fail for the *n*-pentyl group and larger. Also, deviations between our results and ion beam data start to occur for reactions which proceed through intermediates such as R–Co^+–C_5H_{11}. We suggest that H shifts from $-C_nH_{2n+1}$, where $n \geq 5$, need not be β-H shifts but may also be δ- and ε-H shifts, through five- or six-membered ring intermediates. Consider a metal-insertion, ε-H shift mechanism:



When R' = H, the ε-H is a primary H; when R' = CH_3, the ε-H is a secondary H. Thus, we may expect the probability for ε-H shifts to follow the ordering ε-H (n-C_5) < ε-H (n-C_6) < ε-H (n-C_7), etc., i.e., to parallel the trend for β-H shifts. Our data do suggest that the probability of a H shift from n-C_6 is less than from n-C_3, while that for n-C_7 is greater than from n-C_3, suggesting that a H shift from n-C_7 is more probable than from n-C_6. Thus, we suggest that, when a hydrogen atom shifts from an *n*-pentyl group or larger, it cannot be assumed to be a β-H, but may be a combination of β-H, δ-H, and ε-H shifts. It is interesting to note that, in previous studies of alkanes, γ-H shifts (via four-membered ring intermediates) have been considered, but ruled out[3a] while δ-H shifts (via five-membered ring intermediates) from alkyl groups have been suggested as being possible, and consistent with labeling studies.[3d] Thus, we may expect deviations in the results of studies of thermal energy Co^+ ($kT = 0.03$ eV, $T = 298$ K) when compared with that of Co^+ (0.5 eV kinetic energy) in an ion beam, since the intermediates formed by the ion with the higher kinetic energy should have shorter lifetimes. That is, in the work of Beauchamp et al. on Co^+ with alkanes, intermediates of the type R–Co^+–C_5H_{11} may react predominantly by β-H shifts from the *n*-pentyl group, while in the ICR experiments, longer lived in-

---

[23] Tsarbopoulos, A.; Radecki, B. D.; Allison, J. American Society for Mass Spectrometry Meeting, San Antonio, TX, 1984, p 225.

termediates may be able to achieve cyclic forms conducive to δ- and ϵ-H shifts. Future studies of the chemistry of transition metal ions with larger, labeled alkanes should provide further insights into this area.

Summary

The purpose of the present study was to examine the effect of the chain length in the reaction pathways of Co^+ with some monofunctional organic molecules and to suggest an ordering for preferred site of attack of skeletal bonds. In the study of a series of straight-chain alkyl chlorides and alcohols, increases in the chain length lead to a rich chemistry in both cases.

Metal ions such as Co^+ react with longer chain *n*-alkyl chlorides and normal alcohols by mechanisms similar to alkanes, i.e., by inserting into the skeletal C–C bonds. This leads to the formation of metal–olefin complexes in the case of *n*-alkyl chlorides and metal ion-small alcohols complexes in the case of alcohols. This is consistent with the proton affinity rule[9] for competitive ligand loss.

Metal insertion into the polar bonds of C–OH and C–Cl in larger alcohols and alkyl chlorides is not a major pathway, as it is for the small alkyl chlorides and alcohols ($n < 4$).

Long-chain alkyl chlorides exhibit some similarities with alkanes concerning the ordering (pattern) for preferred site of insertion by Co^+. For alcohols, the increase in the chain length has a more "dramatic" effect on the reaction products. Since PA(alcohols) > PA(alkyl chlorides), there is a relatively strong initial cobalt ion–alcohol interaction on complexation. A mechanistic sequence consisting of a metal–carbon atom interaction via the formation of cyclic five- *or* six-membered ring intermediates and a further insertion into the skeletal C–C bonds which come into close proximity with the metal accounts for most of the products observed.

Since the initial interaction between Co^+ and alkyl chlorides is less than that with alcohols, we do not see the complexation/five-or-six-membered ring intermediate process playing as important a role for the chloroalkanes. The effect due to the presence of the chlorine is less dominant than that of the OH group. Also, when complexation of Co^+ to the chlorine atom of an alkyl chloride occurs, metal insertion into the C–Cl bond occurs, favored by the strong Co^+–Cl bond. Since the Co^+–OH bond[2d] is weaker than the Co^+–Cl bond,[24] and C–OH bonds are stronger than C–Cl bonds,[14] attack at the functional group is less important on complexation for the alcohols.

Concerning the mechanistic step of the β-H shift following metal insertion into a C–C bond and the formation of an intermediate containing two alkyl groups bound to the metal center, the alkyl group carrying no functional group usually provides the H that shifts onto the metal center, with the exception of the $-(CH_2)_4OH$ group.

Further studies of Co^+ with bifunctional organic molecules (halo alcohols and dihaloalkanes) containing two or more carbon chains are now under way, in order to better understand how the chain length affects the reactivity and the preferred site of attack.

Registry No. C_3H_7Cl, 540-54-5; C_3H_7OH, 71-23-8; C_4H_9Cl, 109-69-3; C_4H_9OH, 71-36-3; $C_5H_{11}Cl$, 543-59-9; $C_5H_{11}OH$, 71-41-0; $C_6H_{13}Cl$, 544-10-5; $C_6H_{13}OH$, 111-27-3; $C_7H_{15}Cl$, 629-06-1; $C_7H_{15}OH$, 111-70-6; $C_8H_{17}Cl$, 111-85-3; $C_8H_{17}OH$, 111-87-5; CO^+, 16610-75-6.

---

[24] From the appearance potential of $CoCl^+$ ion obtained from the mass spectral studies of $Cl_3SiCo(CO)_3PF_3$ and $Cl_3SiCo(CO)_2(PF_3)_2$ (18.7 ± 0.4 and 18.9 ± 0.5 eV, respectively)[25] and using the values of $\Delta H_f(CO) = -26.4$ kcal/mol,[21] $\Delta H_f(PF_3) = -219.6$ kcal/mol,[21] $\Delta H_f(SiCl_2) = -37.66$ kcal/mol,[26] $\Delta H_f(Cl_3SiCo(CO)_3PF_3) = -548 \pm 10$ kcal/mol[25] and $\Delta H_f(Cl_3SiCo(CO)_2(PF_3)_2) = -748 \pm 10$ kcal/mol,[25] we can estimate the bond strength between Co^+ and Cl, $D(Co^+{-}Cl) = 91.4 \pm 19.2$ kcal/mol.

[25] Saalfeld, F. E.; McDowell, M. V.; MacDiarmid, A. G.; Highsmith, R. E. *Int. J. Mass Spectrom. Ion Phys.* **1972**, *9*, 197.

[26] Sinke, G. C. "Thermodynamic Properties of Combustion Products, JANAF, Thermochemical Data; Dow Chemical Co.: Midland, MI, 1965.

Surface Photochemistry: CdS-Mediated Dimerization of Phenyl Vinyl Ether. The Dark Reaction[1]

Mohammad Ilyas and Paul de Mayo*

Contribution from the Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7, Canada.

Received March 8, 1985

Abstract: The dimerization of phenyl vinyl ether can be induced by light in the presence of CdS. We report here that certain samples of CdS induce the same cycloaddition in the dark, the reaction being attributed to the presence in the CdS of acceptor-type surface states. These surface states could also be produced by treatment of an inactive CdS specimen with sulfuric acid or by the coadsorption of the electron acceptors maleic anhydride and tetrachlorophthalic anhydride. Neither CdS particle size, surface area, nor crystal structure (cubic, hexagonal, or polytype) appeared to be significant factors in the dimerization.

Photochemical reactions involving electron transfer at semiconductor surfaces have been for the last few decades, and continue to be, an area of intensive research. Much of this work has been motivated by the desire to achieve the light-induced generation of fuel (e.g., the photolysis of water). Cadmium sulfide, having a small band gap and good spectral response in the visible region, has been an important focus of attention. However, more attention has been paid to the development of solar cells (the photoproduction of hydrogen) and much less to the development of the use of CdS for other organic electron-transfer reactions. Among the few photoreactions using CdS dispersions reported, other than oxidation/reduction,[2] are the dimerization of phenyl vinyl ether[3] (PVE) and the cis–trans isomerization[4] of styrene derivatives. It was in connection with the former that a slow, but significant, *dark* reaction occurred which could be used as a probe of the physical condition of the CdS dispersion utilized. The present contribution reports how modification of the surface or the purity

---

[1] Publication No. 343 from the Photochemistry Unit, University of Western Ontario.

[2] (a) Kanno, T.; Oguchi, T.; Sakurai, H.; Tokumaru, K. *Tetrahedron Lett.* **1980**, *21*, 467. (b) Saeva, D. F.; Oline, G. R. *J. Chem. Soc., Chem. Commun.* **1980**, 401.

[3] (a) Draper, A. M.; Ilyas, M.; de Mayo, P.; Ramamurthy, V. *J. Am. Chem. Soc.* **1984**, *106*, 6222. (b) Barber, R. A.; de Mayo, P.; Okada, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1073.

[4] (a) Al-Ekabi, H.; de Mayo, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1231. (b) Submitted for publication.

0002-7863/85/1507-5093$01.50/0