EFFECTS OF FUNCTIONALITY AND CHAIN LENGTH
IN
GAS PHASE ORGANOMETALLIC CHEMISTRY

By

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ABSTRACT

EFFECTS OF FUNCTIONALITY AND CHAIN LENGTH IN GAS PHASE ORGANOMETALLIC CHEMISTRY

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The gas-phase chemistry of ions of the type Co^+, $CO(CO)_x^+$ and $Co(CO)_yNO^+$ with 1-chloro-n-alkanes, n-alcohols, n-chloro-1-alcohols and 1-bromo-n-chloro-alkanes with alkyl chain length varying from two to eight carbon atoms is presented. The proton affinity rule (a model determining which neutrals will be lost from each possible reaction intermediate) and collision-induced dissociation (CID) experiments are used to provide insights into mechanisms and ionic product structures.

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 reactions of the $Co(CO)_x^+$ ions with the series of chloroalkanes and alcohols resemble those for Co^+, while the reactions of the $Co(CO)_yNO^+$ ions are dominated by ligand substitution reactions.

Bifunctional molecules exhibit a much richer chemistry with the metal ions studied than do the monofunctional compounds. In chloroalcohols and bromochloroalkanes, metal insertion into the polar C-X (X=OH,Cl,Br) bond and the internal C-C bonds is observed for Co^+, with the reaction products being "unique" to the combination of functional groups and chain length. Prediction of the reaction products of Co^+ with these bifunctional compounds based on the known chemistry of each functional group is not possible. That is due to the simultaneous interaction of Co^+ with both functional groups in the reaction intermediates, which has a "directing" effect on the metal insertion site. A mechanistic model, involving bicyclic intermediates is used to explain the metal ion preference for insertion into internal C-C bonds as the chain length increases.

Metal insertion into C-C bonds is also observed for the CoL_x^+ ions with the series of chloroalcohols, probably due to the additional energy in the reaction intermediate due to the strong $Co^+ \cdots OH$ interaction.

This is dedicated to my parents for all the love and encouragement they have given me in my life.

This is especially dedicated to the person who always believed in me and encouraged me to be the best person I could possibly be, my MOTHER.

Αυτο το διδακτορικο αφιερωνεται στους γονεις μου για ολη την αγαπη και την υποστηριξη που μου εχουν δωσει μεχρι τωρα.

Ιδιαιτερα στη **ΜΗΤΕΡΑ** μου που παντα με παροτρυνε να δινω τον καλυτερο εαυτο μου σε ο,τι εκανα, επιδιωκων το "τελειο".

As you set out for Ithaka
hope your road is a long one,
full of adventure, full of discovery....

Keep Ithaka always in your mind.
Arriving there is what you're destined for.
But don't hurry the journey at all.
Better if it lasts for years,
so you're old by the time you reach the island,
wealthy with all you've gained on the way,
not expecting Ithaka to make you rich.

Ithaka gave you the marvelous journey.
Without her you wouldn't have set out.
She has nothing left to give you now.

And if you find her poor, Ithaka won't have fooled you.
Wise as you will have become, so full of experience,
you'll have understood by then what these Ithakas mean.

From "ITHAKA" by C.P. Cavafy

ACKNOWLEDGEMENTS

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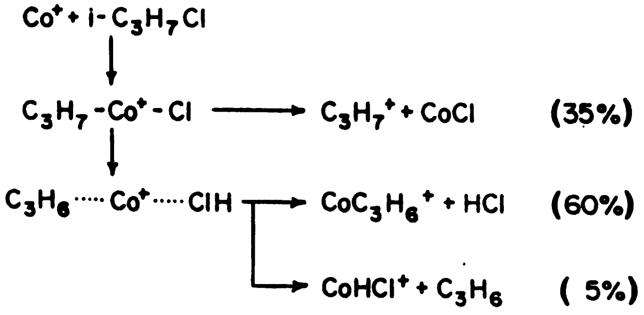
CHAPTER 1

INTRODUCTION

In the past several years a considerable number of studies concerning the gas phase chemistry/reactivity of metal and metal-containing ions with organic molecules has appeared in the literature. These studies, performed using ion cyclotron resonance (ICR) spectrometry [1-4], fourier transform mass spectrometry (FTMS) [5-8] and ion beam techniques [9-12] have provided information on the activation of different bonds in organic molecules by metal ions without the presence of the complicating solvent effects. Thermodynamic, kinetic and mechanistic information concerning the gas phase organometallic chemistry of metal ions can be obtained from these studies. These studies can be also useful in the development of metal ions as chemical ionization (CI) reagents in mass spectrometric analysis [13,14], due to the specific chemistry of metal ions with organic molecules containing various functional groups.

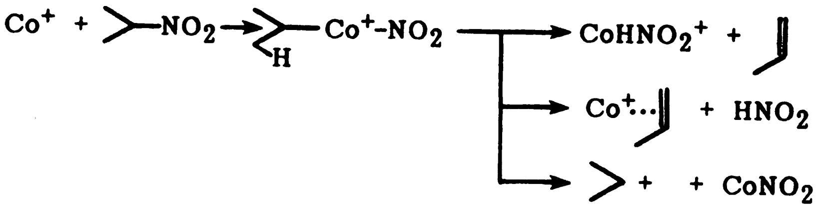
Most of the work done to date involves first row transition metal and alkali metal ions with a variety of molecules representative of the basic organic functional groups. Thus the reactions of transition metal ions with organic species such as alkenes [15-18], alkyl halides [2,19], alcohols [19], amines [20,21], aldehydes [3,13,22], ketones [3,13,22], carboxylic acids [13,23], esters [13], ethers [3,24], sulfides [25], mercaptans [23] and nitroalkanes [26], have been studied, along with the reactions of a variety of metal ions with alkanes [9-11,27-30].

In the early work in this area, Allison and Ridge [31] 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^+, Ni^+ with alkyl halides and alcohols. For example, Co^+ (which can be formed by electron impact on $Co(CO)_3NO$) reacts with 2-chloropropane [19] by first inserting into the polar bond (here C-Cl), followed by either a charge transfer process to form $C_3H_7^+$, or a β-H shift forming two ligands, propene and HCl bound to the metal center. These ligands compete for sites on the metal and subsequent dissociation of the $Co(HCl)(olefin)^+$ complex accounts for the major fraction of the observed products

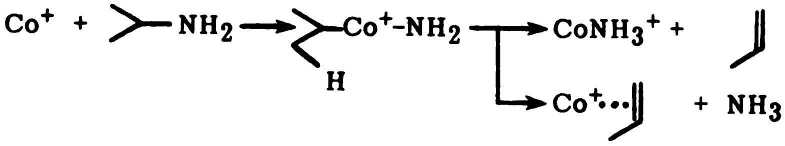


This mechanism can be used to explain dehydrohalogenation of alkyl halides as well as dehydration of alcohols [19]. In the case of alcohols, metal ion insertion into the C-OH bond induces H_2O elimination. For example, the Co^+ ion reacts with ethanol via insertion into the C-OH bond, followed by a β-H shift to give (ethene)$Co^+(H_2O)$ complex which then undergoes competitive ligand loss to give $CoC_2H_4^+$ (87%) and CoH_2O^+ (13%).

In the studies which followed, the above mechanism has proven to be useful in explaining the observed products in the metal ion chemistry of many types of monofunctional organic molecules. In the chemistry of Fe^+ with small ketones [3,13], metal insertion into each C-CO bond leads to the majority of the products. Nitroalkanes also react with metal ions exhibiting products indicative of the mechanism described above. For example Co^+ appears to insert into the C-N bond of 2-nitropropane, giving rise to 36% of the products [26]:



Metal insertion into the C-C bond, as well as into the C-H bond account for the rest (64%) of the products observed. Amines, being polar compounds as well, were expected to undergo similar reactions with metal ions, i.e., metal ion insertion into the polar C-N bond. For instance one might predict that Co^+ would react with 2-aminopropane to give the $CoNH_3^+$ and $CoC_3H_6^+$ products:



However, products indicative of Co^+ insertion into the C-N bond of primary amines are *not* observed. Instead, cobalt ions react with primary amines by inserting into the N-H, C-H and C-C bonds resulting in the elimination of H_2, small alkanes and small alkenes [20]. In the case of 2-aminopropane products corresponding to H_2 and CH_4 elimination as well as loss of the neutral CoH, have been reported [20]. The failure of Co^+ to insert into the $C-NH_2$ bond has been suggested to be due to a weak Co^+-NH_2 bond, which makes the formation of the metal insertion intermediate $R-Co^+-NH_2$ an endothermic process.

Therefore primary amines are a unique type of monofunctional organic molecule, where Co^+ does not insert into the polar bond of these molecules ($C-NH_2$). Instead it inserts into C-H, N-H and C-C bonds; thus exhibiting a chemistry which parallels that observed for alkanes, rather than that observed for other polar compounds. In compounds with *no* polar bonds, like alkanes and alkenes, metal ion insertion into the C-H and C-C bond is the initial mechanistic step accounting for all the products observed [9,16].

From these examples and all the work done to date on similar organometallic systems, it is shown that metal ions such as Co^+ react in specific ways with organic molecules. The reaction products observed reflect functionality and structure of the organic species, and they can be predicted if the initial sites of attack are known. The specific chemistry of metal ions with organic molecules is the basis for a new approach to chemical ionization mass spectrometry (CIMS); i.e., the use of metal ions as CI reagents [13,14,32].

In CIMS, a technique that was first described by Munson and Field (1966) [33], ions characteristic of the sample molecules are formed in ion/molecule reactions between reagent ions and the sample. The reagent ion may be a molecular ion, fragment ion or product of an ion/molecule reaction between a primary ion and a reagent gas molecule. In CH_4-CIMS the reagent ions (CH_5^+ and $C_2H_5^+$) undergo ion/molecule reactions with the sample to form the protonated molecular ion MH^+. The amount of fragmentation observed in CIMS is less than that observed in electron impact mass spectrometry (EIMS) and depends on the type of reagent ion that is used. Thus, the search for reagent ions that will give information concerning the presence of particular functional groups or molecular geometries is an active area of research.

From the previous discussion, it seems that metal ions such as Co^+ could be used as CI reagent ions. The generation of some simple rules for Co^+-CI mass spectral interpretation is preferable to generating a Co^+-CI mass spectral library for compound identification. The first step in identifying "rules" for Co^+-CI is the study of molecules representative of all of the basic organic functional groups. But in most of the mass spectrometric analyses today, complicated multifunctional molecules are involved rather than simple monofunctional molecules.

A major research effort in our laboratory is the study of the chemistry of ionic metal centers with multifunctional compounds [1,14,34,35]. In order to generate rules for Co^+ reactivity with multifunctional compounds and furthermore evaluate the eventual utility of metal ion chemical ionization, it must be determined how the products of the reaction between a metal ion and an organic compound containing more than one functional group are related to the reactant molecule. If Co^+ reacts with a saturated hydrocarbon skeleton containing, e.g., a Cl and an OH group, one or more of the following may be observed:

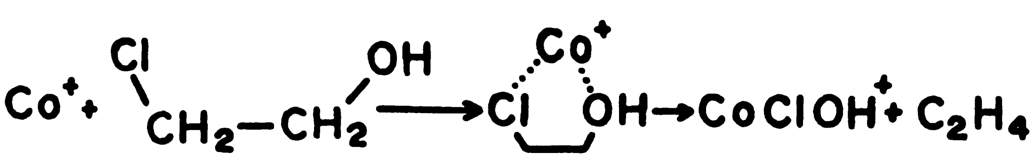
(1) Products representative of alcohol reactions and products typical of alkyl halide reactions are formed.

(2) Products only typical of one functional group are formed (indicating that

Co$^+$ would show a preference for one functional group over another).

(3) Products that are unique to this combination of functional groups are formed.

Reactions exemplary of all three possibilities have been observed [14,34,35]. In a previous report from our laboratory [14], bifunctional compounds with both groups in close proximity were studied. In this case, the interaction of both functional groups with the reactant metal ion is geometrically accessible and apparently occurs, e.g.



The first part of this dissertation deals with bifunctional compounds where the functional groups are removed from each other, i.e., 1,4-bisubstituted n-butanes. Since the four-carbon chain is too long for both groups to easily interact with the metal ion simultaneously (a seven-membered ring intermediate would be involved), it can be determined whether Co$^+$ exhibits a preference for one functional group over another. A simple "ligand competition" model along with collision-induced dissociation analysis will be used in order to provide insights into the ionic product structures. Determination of product ion structures may facilitate the elucidation of reaction mechanisms and probe additional insights into the mechanistic sequence of metal insertion/β-H shift/competitive ligand loss.

In the second part of this dissertation each step of this mechanism will be examined, as it applies to the chemistry of Co$^+$ with a series of

1-chloro-n-alkanes and n-alcohols when the alkyl chain length varies from three to eight carbon atoms. These chain length studies can provide insights into the metal insertion step, which appears to be the least understood step. For example, why does Co^+ not insert into the C-C bond in ethanol or i-propanol but does in the case of n-butanol [34,35]? Why does Co^+ only insert into the C-Cl bond in ethyl, n-propyl and n-butyl chlorides [36]? Thus if the three mechanistic steps (metal insertion/β-H shift/competitive ligand loss) are sufficiently understood, the product distributions for bimolecular organometallic reactions could be predicted a priori, and the Co^+-CI mass spectra could be easily understood.

The third aspect of this dissertation will deal with the chemistry of Co^+ with bifunctional organic molecules (halo-alcohols and dihaloalkanes) containing two to six carbon chains. In these experiments the combined effect of the chain length and the functional group on the chemistry exhibited by the metal ion (Co^+) was examined and some additional rules for the interpretation Co^+-CI mass spectra of bifunctional compounds were determined.

In most of the studies to date, the emphasis has been placed on the characterization of the gas phase chemistry of the bare metal ions, M^+, with a variety of functional groups. Whenever metal ions M^+ are generated by electron impact on volatile metal carbonyls, $M(CO)_x{}^+$ ions are formed as well. In the early experiments of this type, these ions, i.e., metal ions bound to one or more CO groups, exhibited very simple chemistries, reacting almost exclusively by ligand substitution [19,37]. In this dissertation, the discussion of the chemistry of Co^+ with each compound is followed by a discussion of the chemistry of the cobalt-containing ions $CoL_x{}^+$ (which are formed by electron impact on $Co(CO)_3NO$) with that compound. By comparing the chemistries of Co^+ and $CoL_x{}^+$ with the organic compounds studied, the effects of the CO and NO ligands on the chemistry exhibited by Co^+ will be determined (CO and NO are both very important ligands in catalytic reactions).

CHAPTER 2

EXPERIMENTAL

I. ION CYCLOTRON RESONANCE SPECTROMETRY

Ion cyclotron resonance (ICR) spectrometry is a relatively new technique (less than three decades old) which has been developed for studying ion/molecule reactions in the gas phase, and has given rise to an extraordinary expansion of our knowledge of ion properties. A number of reviews are available on this technique [38-46]. Even though the history of the ICR technique is considered to have begun with the introduction by Baldeschwieler _et al._ of the drift-cell ICR spectrometer in 1966, two earlier instruments were based on the same basic principle. The first was the Omegatron developed by Sommer, Thomas and Hipple, which was used to measure m/e for the proton [47,48]. The second was the resonance detection instrument developed by Wobschall _et al._ [49,50]. It had a solenoidal magnet and used for collision-rate studies of atmospheric gases. Neither instrument has been of importance in the development of ICR Spectrometry for studying ion/molecule reactions.

Figure 1 shows a block diagram of an ICR spectrometer. The ICR cell is shown in detail in Figure 2. It is a three section cell, consisting of an ion source, analyzer and collector, and is placed between the poles of an

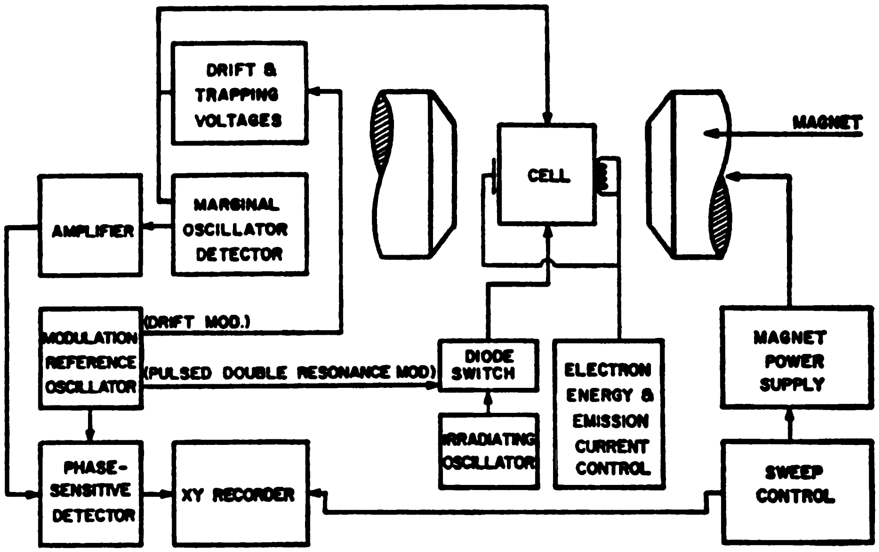


Figure 1 Block Diagram of ICR Spectrometer

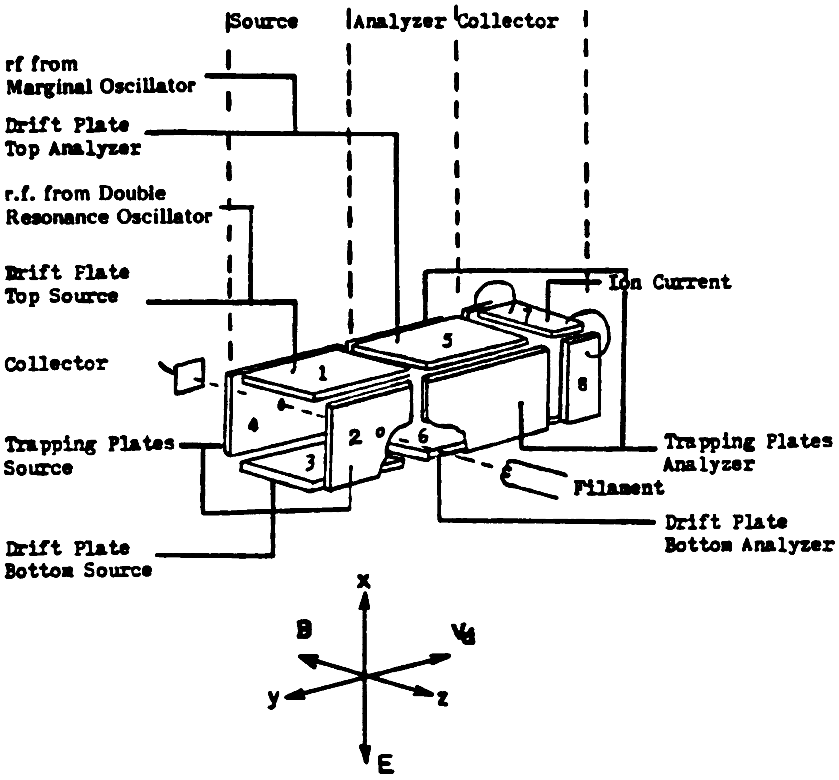


Figure 2 The ICR Cell

electromagnet of magnetic field strength B [51], directed as shown in Figure 2. Electrons emitted from a hot filament (usually rhenium or tungsten or mixture of both), are accelerated toward the near side of the cell (plate 2) by applying a negative potential on the filament, forming a collimated electron beam by the magnetic field B. The electron beam passes through the cell and falls on the collector plate, where it is measured as the emission current, which is regulated by the emission controller (Figure 1). A small fraction of the electron beam is responsible for the ionization of the molecules in the ion source region of the ICR cell. The ionizing energy is determined by the potential difference between the filament and the side of the cell (plate 2).

Ion motion parallel to $\vec{B}$ is unrestricted. The ions are prevented from leaving the cell in the source and analyzer regions, by applying a small potential ($\leq$ 0.5 V) to the trapping plates (e.g., plates 2 and 4 in the source region). This voltage, called trapping voltage (positive for cation experiments, negative for anion experiments), creates a potential well along the magnetic field direction (Z) and prevents the ions from hitting the walls.

II. DYNAMICS OF NONRESONANT IONS

For a moving ion of mass m, charge q and velocity $\vec{v}$ perpendicular to $\vec{B}$, the force on the ion is give by the vector equation:

$$\vec{F} = q(\vec{V} \times \vec{B}) \tag{1}$$

Here $\vec{V} \times \vec{B}$ is the vector product of $\vec{V}$ and $\vec{B}$, a vector at right angles to both, whose magnitude is the product of the magnitudes of $\vec{V}$ and $\vec{B}$ times the sine of the angle between them [52,53]. Therefore if the ion is initially moving in a plane normal to B, then F is also in this plane and normal to the direction of motion. The motion of the particle is thus restricted to a circular orbit such that:

$$\frac{mv^2}{r} = q(v \times B) = qvB \tag{2}$$

where r is the radius of the orbit. If ω_c is the angular frequency (or cyclotron frequency) of the ion in rad/sec, then equation (2) leads to:

$$\frac{mv}{r} = m\omega_c = qB$$

and

$$\omega_c = \frac{qB}{m} \tag{3}$$

This basic cyclotron equation shows that ω_c, and hence the time required per revolution, is independent of the velocity of the particle v, whereas the radius of the orbit is directly proportional to v according to equation (4):

$$r = \frac{mv}{qB} \tag{4}$$

Rearrangement of equation (3) gives an expression for the frequency f_c.

$$f_c = \frac{\omega_c}{2\pi} = \frac{qB}{2\pi m}\left(\frac{\text{cycles}}{\text{sec}}\right)$$

or

$$\frac{m}{q} = \frac{B}{2\pi f_c} \tag{5}$$

Equation (5) shows that, for a constant f_c, m/q varies linearly with B.

The ions that are produced in the source are made to drift from the source to the analyzer region of the ICR cell by applying a potential difference across the drift plates (1,3,5,6) of the cell. The electric field (E) applied between the plates is perpendicular to the magnetic field and the force exerted on the charged particle is given by the following equation:

$$F = qE + q(V \times B) \qquad (6)$$

This force causes the ion to move in a direction perpendicular to both the magnetic and electric field, with a drift velocity given by

$$v_d = \frac{E_d}{B} \qquad (7)$$

where E_d is the electric field intensity, i.e., the quotient of the potential difference by the distance between plates. The direction and magnitude of v_d are independent of the mass of the particle and the sign of the charge.

III. CYCLOTRON RESONANCE DETECTION

The detection of ions in ICR Spectrometry is done by incorporating the top and bottom plates of the analyzer region into the capacitive element of the resonance circuit of the marginal oscillator (Figure 3). Ions are detected when their cyclotron frequency (ω_c) given by equation (3) equals the marginal oscillator frequency (resonance condition, i.e., $\omega_c = \omega_{m.o.}$). An ion in resonance absorbs power from the field, resulting in a change in the resistive impedance of the resonant circuit which is reflected by a change in the radio-frequency voltage level of the marginal oscillator. As an ion absorbs energy, it gains speed, and in order to remain in resonance its cyclotron orbit increases in radius during the time it spends in the analyzer region (Figure 4).

The signal/noise ratio (S/N) of the marginal oscillator output is enhanced by signal modulation and phase-sensitive detection (lock-in amplifier).

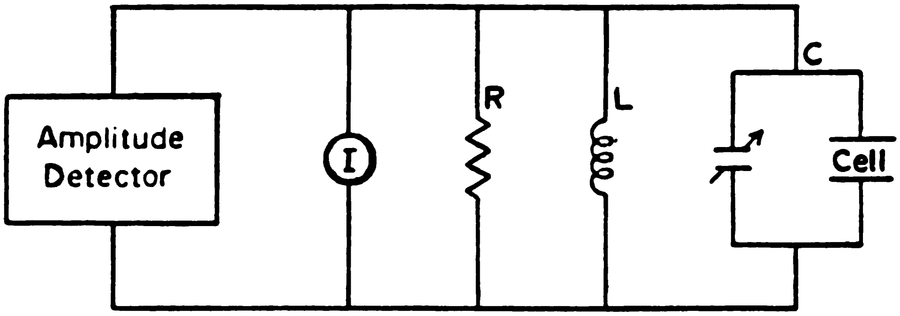


Figure 3 LC Tank Circuit of Marginal Oscillator Detector

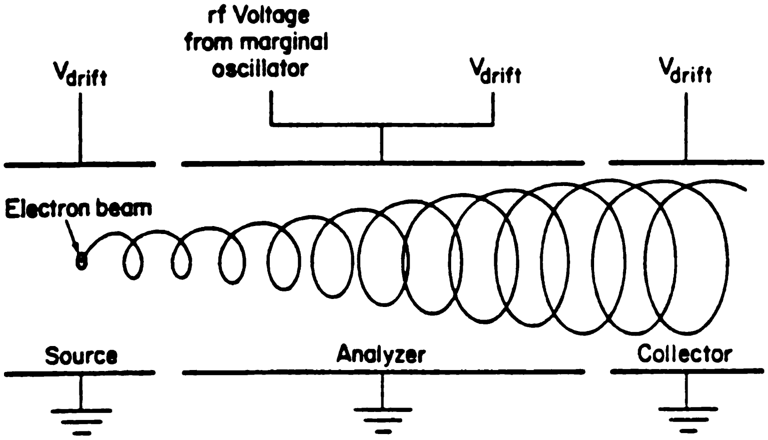


Figure 4 Motion of a Typical Ion Through the Drift ICR Cell

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Modulation schemes can be classified according to whether they perturb the resonance condition or effect a change in the density of ions in the analyzer region. The former includes frequency modulation of the marginal oscillator and magnetic field modulation [45]. The latter includes modulation of the drift voltage, trapping voltage [41], electron beam current [54], electron energy [55] and the highly specific double resonance technique [38].

In an ICR experiment the usual way of bringing ions of different masses into resonance with the marginal oscillator is by keeping the marginal oscillator at a constant frequency and scanning the magnetic field. It is convenient to operate the marginal oscillator at a frequency of ≈ 153 kHz, since, at that frequency a change of 100 Gauss (0.01 T) in B corresponds to a change of one atomic mass unit (assuming unit charge).

$$f_c = \frac{1.6022 \times 10^{-19}\ \mathrm{C} \times 0.01\ \mathrm{T}}{2 \times 3.1416 \times 1\mathrm{u} \times 1.6604 \times 10^{-27}\ \mathrm{kg/u}} = 153.57\ \mathrm{kHz}$$

Lower marginal oscillator frequencies are used in order to increase the mass range; however mass resolution decreases with increasing mass range.

IV. ION CYCLOTRON DOUBLE RESONANCE

A unique feature of ICR Spectrometry is the correlation that can be determined between a product ion and the reactant ion that formed it in an ion/molecule collision of the type:

$$A^+ + C \longrightarrow B^+ + D \qquad (1)$$

This is done by adding energy through a variable radiofrequency oscillator to possible reactant ions, while the product ion is in resonance with the marginal oscillator detector (ion cyclotron double resonance - ICDR) [38]. For an ion in resonance at a certain value of B, equation (3) gives: $m\omega_c$ = constant. In order to bring ions of different mass m' into resonance (at the same value of B), the appropriate value of ω_c' has to be applied such that $m\omega_c = m'\omega_c'$. For the reaction (1) this can be rewritten as:

$$m_B(\omega_c)_B = m_A(\omega_c)_A \tag{8}$$

By adding energy to A^+, a change in the amount of product B^+ may be observed through a change in the marginal oscillator response. Since $(\omega_c)_B$ is known (usually is ≃ 153 kH_3), it is easy to predict the frequency $(\omega_c)_A$ at which the intensity of B^+ will decrease to indicate a unique reactant/product ion pair. While double resonance experiments provide a means for identifying ion/molecule reactions, they do not facilitate in determining the product ion distributions (branching ratios).

A useful technique for the determination of product ion distributions is the ion-ejection technique [56]. Ions are excited, using the double-resonance oscillator, with a strong burst of energy at their ω_c. These ions are excited until r becomes greater than the dimensions of the ICR cell, thus ejecting the ions out of the experiment (cell). In the ion-ejection technique the link between reactant and product ion appears as a decrease in intensity of a monitored product ion when various reactant ions contributing to its formation are consecutively ejected by a frequency-swept ejection field. The observed decrease in each case is equal to the contribution of the ejected reactant to the product.

V. DYNAMICS OF RESONANT IONS

In both the detection of ions and their irradiation in the double resonance experiment, they are interacting with an rf electric field. The force on the ion will be:

$$F = \frac{E_{rf} \cdot q}{2} = m \cdot a \tag{9}$$

where E_{rf} is the amplitude of the electromagnetic wave and a is the acceleration of the ion.

The instantaneous power A absorbed by a single ion, assuming ion/neutral collisions, is defined by:

$$A(t) = F \cdot v = F \cdot \int_0^t a dt = \frac{q^2 E_{rf}^2 t}{4m} \tag{10}$$

where v is the velocity of the ion after it has been in resonance for time t.

The average power absorption for an ion, being in resonance, in a rf field is:

$$A(t) = \overline{A(t)} = \frac{1}{\tau} \int_0^\tau A(t) dt = \frac{q^2 E_{rf}^2 \tau}{8m} \tag{11}$$

Thus the power absorbed by an ion depends on the residence time of the ion in the rf field (τ), and also depends inversely on its mass.

VI. SIGNAL INTENSITIES

The simple resonance line intensity for an ion (i.e., the power absorption for that ion at resonance), can be calculated by averaging power absorptions occurring in each time element in the analyzer over all ions of that type. The signal intensity is thus:

$$I_i = \int A_i(t)\, Q_i(t)dt \qquad (12)$$

where $A_i(t)$ is the power absorbed per ion and $Q_i(t)$ is the current of all ions of type i.

For a nonreactive ion, the signal intensity becomes,

$$I_i = \frac{Q_i q^2 E_{rf}^2 \tau^2}{8m_i} \qquad (13)$$

where τ is the ion drift time in the analyzer region. An expression for τ is given by equation (14) (by combining equations (3) and (7) with the $\tau = l/v_d$ expression):

$$\tau = \frac{lB}{E_d} = \frac{l m_i \omega}{q \cdot E_d} \qquad (14)$$

where l is the length of the analyzer region, E_d is the electric "drift field" intensity and ω is the oscillator frequency ($\omega = \omega_c$). Thus, the following expression is obtained by inserting equation (14) into equation (13):

$$I_i = \frac{Q_i m_i \omega^2 l^2 E_{rf}^2}{8E_d^2} \qquad (15)$$

It can be seen that at low pressure, the peak height at constant rf frequency and swept magnetic field increases linearly with ion mass, so that in order to obtain a quantitative mass spectrum the peak heights must be divided by the corresponding mass. Also, the peak heights and the spectrometer sensitivity increase with the square of the operating frequency ω.

At higher pressures, the ions undergo collisions with neutrals. The energy absorbed by the ion from the rf field is rapidly dissipated to the neutral molecules and a steady state is rapidly reached in which energy gain from the rf field is balanced by energy loss due to collisions. Equation (10) still applies, but t must now be taken as the collisional energy relaxation time.

Detailed treatments on the effect of collisions on the ion motion and on the power absorption expression are available [45,57]. These are necessary in obtaining accurate reaction kinetic data from the ICR mass spectra.

VII. EXPERIMENTAL SET-UP

All experiments were performed on an ion cyclotron resonance spectrometer of conventional design that was built at Michigan State University. The three section cell is 0.88 in. x 0.88 in. x 6.25 in. The source region is 2.00 in. long, the analyzer region is 3.75 in. long, and the collector is 0.50 in. long. Ions are formed in the source by electron impact with 70-eV electrons. The electron filament is emission regulated. The filament controller and plate voltage controller for the ICR cell were designed and constructed at MSU. The instrument is operable in the pulsed or drift ICR modes. Data in this dissertation were obtained under normal drift-mode conditions by using trapping voltage modulation and phase-sensitive detection. The marginal oscillator detector is based on the design of Warnick, Anders and Sharp [58]. A Wavetek Model 144 sweep generator is used as the secondary oscillator in the ion cyclotron double resonance (ion ejection) experiments, performed to identify precursors of ion/molecule reaction products. The ICR cell is housed in a stainless steel vacuum system and is situated between the polecaps of a Varian 12 in. electromagnet (1.5 in. gap). The electromagnet is controlled by a Varian V-7800, 13 kW power supply and a Fieldial Mark I Magnetic Field Regulator.

The instrument is pumped by a 4-in. diffusion pump with a liquid nitrogen cold trap and an Ultek 20 L/s ion pump. Samples are admitted from a triple inlet (individually pumped by a 2-in. diffusion pump and liquid nitrogen cold trap) by Varian 951-5106 precision leak valves. Approximate pressures are measured with a Veeco RG1000 ionization gauge.

Tricarbonylnitrosylcobalt (O) was obtained from Alfa Inorganics. 1-butanol, 1-chlorooctane, 4-bromo-1-butanol and 4-chloro-1-butanol were obtained from Alfa Products. 1-chlorobutane, 1-bromobutane, 2-chloro-1-ethanol and 1-bromo-3-chloro-propane were obtained from Chem-Service. 3-chloro-1-propanol, 4-fluoro-1-butanol, 1-bromo-5-chloro-pentane and 1-bromo-6-chloro-hexane were purchased from Columbia Organic Chemicals Co. 1-hexanol, 1-heptanol and 1-chloroheptane were obtained from Eastman Kodak Co. 1-chloropentane, 1-chlorohexane, 6-chloro-1-hexanol and 1-bromo-2-chloro-ethane were obtained from Fluka Chemical Corp. 1-propanol and 1-octanol were obtained from Fisher Scientific Co. The 1-chloropropane was obtained from Aldrich Chemical Co. and the 1-pentanol was obtained from J.T. Baker Chemical Co. The 1-fluorobutane was purchased from Pfaltz and Bauer Inc. The 1-bromo-4-chloro-butane was obtained from Fairfield Chemical Co. and the 5-chloro-1-pentanol was obtained from ICN Pharmaceuticals. All these compounds were analyzed for purity and for particular suspected contaminants by gas chromatography and mass spectrometry. All samples were degassed by multiple freeze-pump-thaw cycles and were used without further purification.

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. (The ion/molecule reaction products following electron impact on $Co(CO)_3NO$ have already been determined [59]). Then ion/molecule reaction products (up to m/z 290) 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 x 10^{-5} torr. The observed reactions are facile and dominant reactions have rate constant within an order of magnitude of the collision frequency. Branching ratios for the reported reactions are accurate to within ±10%.

Collision-induced dissociation (CID) experiments were performed on an Extranuclear triple quadrupole mass spectrometer. In the (CI) ion source, 1:2 mixtures ($Co(CO)_3NO$/sample) are admitted to a total pressure of 3.0 x 10^{-4} torr (measured outside the source in the source housing). Ion/molecule reaction products of interest were mass selected by the first quadrupole and accelerated into the second quadrupole (the CID chamber). The collision gas was argon (typical pressure is 3.0 x 10^{-3} torr). Typical collision energies are in the 10-30 eV (lab) range. The products of collision-induced processes that are formed in the collision chamber are mass analyzed by scanning the second mass filter (third quadrupole) [60]. Under the conditions of these experiments, ions such as $ArCH_3^+$ and $ArOH^+$ are formed. Such products are not included in the tabulated data.

CHAPTER 3

THE CHEMISTRY OF COBALT-CONTAINING IONS WITH MONO AND BISUBSTITUTED n-BUTANES

I. INTRODUCTION

A. Establishment of the Proton Affinity (PA) Rule

The "ligand competition" model has been implied in the literature to date, but not extensively used. In one of the earliest works involving ionic cobalt reactions, the ligand substitution reactions of ions derived from EI on $Co(CO)_3NO$ were studied [59]. Competitive ligand substitution reactions such as:

$$CoNO(H_2O)_2^+ + PH_3 \longrightarrow Co(NO)(H_2O)(PH_3)^+ + H_2O$$

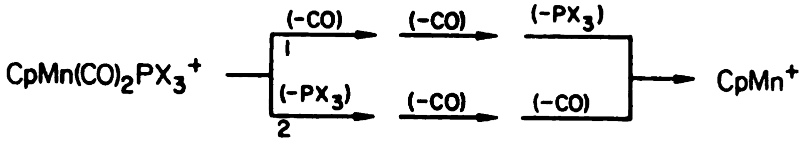
were used to determine the following order of metal-ligand "affinities":

$$NO > NH_3 > PH_3 > AsH_3 > C_2D_4 > H_2O > CO > O_2$$

Three important concepts resulted from this work. First, the order appeared to be independent of the number of ligands on the metal. Second, reactions of the $CoNO(X)(Y)^+$ species did not indicate that the strength of the Co-X interaction depended on the identity of Y (at least not in the context of the ligand substitution reactions studied). Third, the trend reported suggests that the proton affinity (PA) of the ligand reflects its metal ion affinity D(M^+-ligand) (i.e., the strength of the metal-ligand interaction) [61]. (Pertinent proton affinities are given in Appendix A.) Thus in the series shown above, NH_3 has the highest PA (205 kcal/mol) and O_2 has the lowest (100 kcal/mol). Note that only simple, monodentate ligands were studied. There are two notable exceptions to this rule. The NO molecule has a PA of 120 kcal/mol but has a very high bond strength to Co^+. This is expected because NO is (can be) a three-electron donor and cannot be considered in the same category as the other compounds that can only "offer" an electron pair for the interaction with the metal. Also, when H_2O and olefins (C_2H_4) compete for a site on the metal, preference by the metal for the olefin over H_2O is shown, even though, by the proton affinity rule, H_2O should be a slightly better ligand than an olefin such as ethylene. The parallel trend of metal-ligand bond strengths with proton affinities has been discussed for many other transition-metal and metal-containing ions [62-69].

Thus, the model suggested from gas-phase ion/molecule reactions is as follows: If a complex of the type $M\text{-}(L_1)(L_2)(L_3)^+$ is formed with excess energy, that energy can be used to break metal-ligands bonds. The bonds most readily broken are the weakest bonds. Ligands with the lowest metal-ligand bond strength(s) are preferentially lost. This preference can be predicted with knowledge of the proton affinity of the ligands.

This effect has also been noted in the EI mass spectra of organometallic compounds. In a classic review on early work in this area by Müller [70], the fragmentation sequence for organometallic compounds containing several different ligands bonded to a central metal is discussed. Ligands are divided into two groups according to their ease of removal. Group 1 ligands (e.g., CO, N_2, PF_3, C_2H_4) are easily removed. Group 2 (e.g., amines, thioethers, aromatic hydrocarbons) are difficult to remove. Müller discusses these two groups in terms of their donor/acceptor ability [70]. Group 1 represents good acceptor ligands, i.e., species which should exhibit weakened metal-ligand bonds by the presence of a charge on the metal. Group 2 species are good donor ligands. It should be noted that group 1 compounds have lower PA's than group 2. Consider two pathways for fragmentation of $CpMn(CO)_2PX_3$ to form $CpMn^+$:



$Q \equiv$ path 2/path 1

For X = F, Q = 5.57. For X = H, Q = 0.05. Thus, as the PA of PX_3 increases, pathway 1 is favored over pathway 2; i.e., the PX_3 ligand becomes more difficult to remove [70].

Thus, the ligand competition model has been established. Proton affinities of monofunctional π- and n-donor bases appear to provide an indication of the interaction energy between a ligand and a metal ion, with some noted exceptions. The greater the PA of a ligand, the greater the metal ion affinity for that ligand will be. This will be referred to as the "proton affinity rule" in this text. This concept will be used to interpret our results. The evaluation and establishment of such a rule becomes very important in such experiments. As the complexity of reactions in such systems increases, such guidelines will become vital for interpretation of results.

A brief overview of the chemistry of Co^+ and CoL_x^+ with organic molecules similar to those which will be discussed in this dissertation, will provide a basis with which the proton affinity rule can be evaluated.

Beauchamp and Armentrout have reported the chemistry of Co^+ with alkanes such as butane [9].

$$
Co^+ + n\text{-}C_4H_{10} \longrightarrow \left\{ \begin{array}{lll} CoC_4H_8^+ + H_2 & & (29\%) \\ CoC_3H_6^+ + CH_4 & & (12\%) \\ CoC_2H_4^+ + C_2H_6 & & (59\%) \end{array} \right.
$$

The major pathway is insertion into the central C-C bond followed by a β-H atom shift:

$$
\begin{array}{c} CH_3\text{-}CH_2\text{-}Co^+\text{-}CH_2\text{-}CH_3 \longrightarrow (C_2H_4)\text{-}Co^+(H)\text{-}C_2H_5 \longrightarrow \\ \longrightarrow (C_2H_4)Co^+(C_2H_6) \longrightarrow \text{loss of } C_2H_6 \end{array}
$$

Note that Co^+ induces the formation of ethylene and ethane from butane. These two molecules then compete as ligands for Co^+. Only $CoC_2H_4^+$ is observed (C_2H_6 is lost). $CoC_2H_6^+$ would not be an expected product since $PA(C_2H_4) > PA(C_2H_6)$; i.e., it is predicted that ethylene interacts with Co^+ much more than ethane.

In 1979, Allison and Ridge reported the chemistry of Fe^+, Co^+, and Ni^+ (in various states of coordination) with alkyl halides and alcohols [19]. Reactions were discussed in terms of a metal insertion/β-H atom shift sequence that had been proposed [31]. The ions formed by electron impact on $Co(CO)_3NO$ were studied in their reactions with compounds such as ethyl iodide. Co^+ forms the three products shown in reactions (2)-(4) with this compound [19]. Reaction

$$\mathrm{Co^+ + C_2D_5I} \rightarrow \begin{cases} \mathrm{CoI^+ + C_2D_5} & (11\%) & (2) \\ \mathrm{CoC_2D_4{}^+ + DI} & (78\%) & (3) \\ \mathrm{CoDI^+ + C_2D_4} & (11\%) & (4) \end{cases}$$

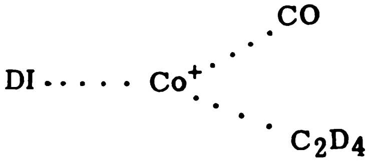
(2), halogen abstraction, is usually observed for alkyl halides. Reaction products in (3) and (4) presumably are formed through a common intermediate:

$$\mathrm{(C_2D_4)\text{-}Co^+\text{-}(DI)}$$

Since PA(HI) < PA(C_2H_4), one would predict DI loss to dominate. This pattern is observed. It is interesting to contrast these reactions to those reported for $CoCO^+$ with C_2D_5I (reaction 5-8). If the products in (5)-(7) are formed

$$\mathrm{CoCO^+ + C_2D_5I} \rightarrow \begin{cases} \mathrm{CoCOC_2D_4{}^+ + DI} & (38\%) & (5) \\ \mathrm{CoC_2D_4{}^+ + DI + CO} & (27\%) & (6) \\ \mathrm{CoDI^+ + C_2D_4 + CO} & (0\%) & (7) \\ \mathrm{CoC_2D_5I^+ + CO} & (35\%) & (8) \end{cases}$$

through the common intermediate



the PA order [PA(DI) < PA(CO) < PA(C_2D_4)] would predict products in (5) and (6) to dominate over products in (7), as is observed.

Also, we would assume that reaction (8) is a simple ligand substitution. That is, the product contains C_2D_5I intact, not as (C_2D_4) and (DI), since CO should not be eliminated to a large extent when DI is retained.

The actual processes that occur for alcohols are not as straightforward. Consider reactions (9)-(12). Products in

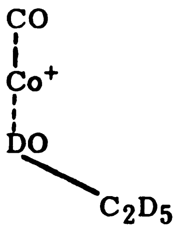
$$Co^+ + C_2D_5OD \longrightarrow CoC_2D_4^+ + D_2O \qquad (87\%) \tag{9}$$

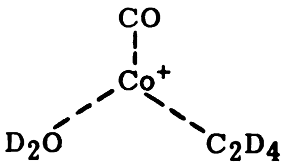
$$ \longrightarrow CoD_2O^+ + C_2D_4 \qquad (13\%) \tag{10}$$

$$CoCO^+ + C_2D_5OD \longrightarrow CoC_2D_5OD^+ + CO \qquad (100\%) \tag{11}$$

$$CoNO^+ + C_2D_5OD \longrightarrow CoNOD_2O^+ + C_2D_4 \qquad (100\%) \tag{12}$$

(9) and (10) presumably come from the common intermediate $Co(H_2O(C_2H_4)^+$. The product distribution does not reflect the relative PA's of H_2O and C_2H_4 (which differ by only 5 kcal/mol) but agrees with the results of Weddle, Allison, and Ridge which specifically indicate $D(Co^+\text{-}C_2H_4) < D(Co^+\text{-}H_2O)$ [59]. Reaction (12) indicates that CoL^+ can also induce the decomposition of ethanol to ethylene and H_2O (both bound to Co^+ in the intermediate complex); however, here only H_2O is retained. This preference for H_2O over olefins apparently occurs when an NO is bound to the metal. Reaction (11) could be interpreted as proceeding through either of these two intermediates:





In either case, the PA rule would predict that CO is the most weakly bound ligand and should be lost. Thus, the development of a consistent rule for the reaction of metal ion with alcohols (i.e., how the atoms of the alcohol are bound to the metal), is not possible because of the relatively high $D(Co^+-H_2O)$. This contrasts to reactions in which the metal ion induced rearrangement of alkyl halides to an olefin and HX is obvious due to the low value of $D(Co^+-HX)$.

In this dissertation, the proton affinity rule will be used to answer a number of questions concerning structural assignment. Suppose we observe

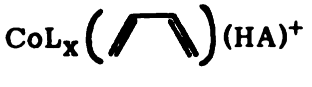
$$CoL_x^+ + A(-CH_2-)_4B \rightarrow CoL_xC_4H_6^+ + HA + HB \tag{13}$$

$$\rightarrow CoL_xC_4H_7A^+ + HB \tag{14}$$

We would assume that reaction (13) proceeds through an intermediate such as

$$Co^+(L)_x(HA)(HB)(C_4H_6)$$

The question is, does the product in (14) have the structure 1 or 2?



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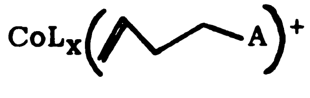


2

Depending on the nature of L,A,B and the value of x, the proton affinity rule will provide insights into the product structure. Note that, to use this approach, all of the ligands in the reaction must be bound to the metal at some time during the reaction and can compete. In some cases, as will be pointed out, reactions will not be able to occur this way but must occur in a stepwise manner. In approaching such questions, the 18-electron rule should presumably not be violated at any point in a proposed mechanism.

B. Utility of CID in Product Ion Structure Elucidation

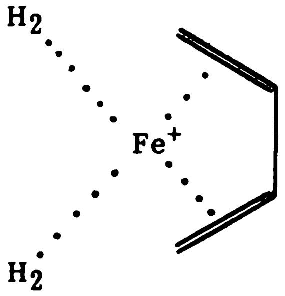
In this work, the collision-induced dissociation (CID) process is used to provide information on product ion structures. The CID process [71,72] involves the collision of a mass-selected ion with a collision gas which transfers internal energy to the ion, inducing fragmentation. The resulting ions contain information about the structure of the selected ion.

The high-energy (3-20 keV) CID process has been demonstrated by using mass-analyzed ion kinetic energy spectrometry (MIKES) with reversed geometry instruments [73,74], while the low-energy (< 100 eV) CID process has recently been utilized, by using triple quadrupole [60] and FT mass spectrometers [5]. Both high-energy and low-energy CID processes have been very useful in ion structure analysis for organic ions [71,72] and have recently been applied to products of organometallic ion/molecule reaction products.

Freas and Ridge [75] reported the high-energy (6 keV collisions with He) CID products of ions of the type $M(C_4H_{10})^+$ formed by

$$MCO^+ + C_4H_{10} \longrightarrow M(C_4H_{10})^+ + CO$$

for M = Fe and Cr. Dramatic differences were noted for the two metals and for isomeric butanes. Products such as $FeC_2H_4^+$ were postulated to result from structures such as $(C_2H_6)Fe(C_2H_4)^+$. Ions such as $FeC_4H_6^+$, however, are probably not indicative of an $FeC_4H_{10}^+$ structure such as



but rather is the result of a collision-induced reaction (CIR), in which additional energy supplied to $FeC_4H_{10}^+$ on the collision prompts the formation of butadiene. Jacobson and Freiser have done an exhaustive CID analysis of metal-olefin complexes from $NiC_4H_8^+$ through $NiC_8H_{16}^+$ under "low"-energy conditions in a Fourier transform ion cyclotron resonance mass spectrometer [29]. These results imply that an ion such as $NiC_8H_{16}^+$ may exist as a collection of structures such as

$$NiC_8H_{16}^+ = Ni(C_3H_6)(C_5H_{10})^+ + Ni(C_4H_8)(C_4H_8)^+$$

If evidence exists for a C_4H_8 ligand bound to a metal ion, CID of that complex always appears to induce H_2 elimination to form a metal-butadiene product. Jacobson and Freiser point out that caution must be exercised in interpreting CID spectra of such ions, since the products represent a mixture of CID and CIR processes [29]. The CIR problem appears to become significant when additional reduction of a ligand is possible. For example, $NiC_6H_{12}^+$ appears to actually exist as $Ni(C_3H_6)_2^+$. The CID spectrum is simple, consisting of $NiC_3H_6^+$ and Ni^+. No further collision-induced reaction for a metal-propene complex would be expected. $Ni(C_4H_8)^+$ is not as simple since butene can be induced to lose H_2 and form a metal-butadiene complex. Thus, the utility of CID in such analyses is still being evaluated. (It should be noted that, in the work done to date, CID products, which are most likely CIR products, tend to be of relatively low intensity.) The limitations must be realized. However, the CID results presented in this work appear to be interpretable and provide useful information in most cases.

II. THE CHEMISTRY

Before presenting the chemistry of the cobalt and cobalt-containing ions with the organic compounds studied, the presentation of the mass spectrum of $Co(CO)_3NO$ is appropriate. At low pressures, the 70 eV EI mass spectrum of $Co(CO)_3NO$ consists of the following ions: Co^+, $CoCO^+$, $CoNO^+$, $Co(CO)_2{}^+$, $CoCONO^+$, $Co(CO)_2NO^+$ and $Co(CO)_3NO^+$. The most abundant ion in the spectrum is the bare metal ion (Co^+).

At higher pressures, these ions react with the neutral $Co(CO)_3NO$ as indicated by the following reactions [59]:

$$\begin{array}{llr} Co(CO)_m{}^+ + Co(CO)_3NO & \longrightarrow Co_2(CO)_{m+2}NO^+ + CO & m=0,1,2 \\ & \longrightarrow Co_2(CO)_{m+1}NO^+ + 2CO & m=0,1,2 \end{array}$$

$$\begin{array}{llr} Co(CO)_nNO^+ + Co(CO)_3NO & \longrightarrow Co_2(CO)_{n+2}(NO)_2{}^+ + CO & n=0,1,2,3 \\ & \longrightarrow Co_2(CO)_{n+1}(NO)_2{}^+ + 2CO & n=1,2,3 \end{array}$$

No evidence for loss of more than two carbonyls or loss of a nitrosyl was obtained. In this work the chemistry of these polynuclear metal ion complexes was not examined.

Tables 1 and 2 contain the reactions of the metal ions derived from $Co(CO)_3NO$ with mono- and bisubstituted n-butanes respectively, along with the branching ratios.

A. Reactions of Cobalt-Containing Ions with n-Butyl Halides

The Co^+ ion reacts with 1-chloro-, 1-bromo-, and 1-fluoro-n-butane to form the butyl cation. Similar results have been reported for other alkyl halides [19], so this product is not unexpected. The cobalt ion also reacts with each of the three halobutanes to form the metal-butadiene complex $Co(C_4H_6)^+$. (The Co^+ ion reacts with a variety of compounds containing a four-carbon chain to produce the (Co^+-butadiene) complex.) The formation of this species from 1-bromo-n-butane implies a lower limit on the metal-ligand bond strength, $D(Co^+\text{-}C_4H_6) > 43.3$ kcal/mol. If the reaction occurs through the intermediate **3** in which all products are bound to the metal,

$$Co^+ + n\text{-}C_4H_9X \longrightarrow \underset{\mathbf{3}}{Co^+(C_4H_6)(H_2)(HX)} \longrightarrow CoC_4H_6^+ + H_2 + HX$$

the proton affinity rule for estimating metal-ligand interactions, i.e., ease of ligand loss, would suggest that H_2 and HX are weakly bound ligands. The bond strengths of multidentate ligands such as butadiene have not been studied to date [76], thus we cannot assume that the $Co^+\text{-}C_4H_6$ interaction is reflected in its PA. Nonetheless, reactions reported here suggest a very strong $Co^+\text{-}C_4H_6$ bond.

The $CoCO^+$ ion reacts with the halobutanes to eliminate HX.

$$CoCO^+ + C_4H_9X \longrightarrow Co(CO)(C_4H_8)(HX)^+ \longrightarrow CoCOC_4H_8^+ + HX$$

Table 1

Reactions of Monosubstituted n-butanes with Ions Derived from $Co(CO)_3NO$[a]

Reactant Ion \ Reactant Neutral	 F	 Cl	 Br	 OH
Co^+	CoF (0.87) $HF + H_2$ (0.13)	CoCl (0.81) $HCl + H_2$ (0.19)	CoBr (0.87) $HBr + H_2$ (0.13)	H_2 (0.21) $H_2 + H_2O$ (0.37) C_2H_4 (0.19) C_2H_6 (0.09) C_4H_8 (0.14)
$CoCO^+$	HF (1.00)	HCl (0.60) C_4H_8 (0.40)	HBr (1.00)	H_2 (0.06) $H_2 + CO$ (0.34) $H_2O + CO$ (0.10) CO (0.31) $C_2H_6 + CO$ (0.04) C_4H_8 (0.08) $C_4H_8 + CO$ (0.07)
$Co(CO)_2^+$	HF + CO (1.00)	HCl + CO (1.00)	HBr + CO (1.00)	$H_2 + CO$ (0.10) $C_4H_8 + CO$ (0.09) CO (0.53) 2CO (0.28)
$CoNO^+$				C_4H_8 (1.00)
$CoCONO^+$				CO (0.80) $C_4H_8 + CO$ (0.20)
$Co(CO)_2NO^+$		CO (0.31) 2CO (0.69)	CO (0.14) 2CO (0.86)	$C_4H_8 + 2CO$ (0.04) $H_2 + 2CO$ (0.12) 2CO (0.84)
$Co(CO)_3NO^+$		2CO (1.00)	2CO (1.00)	$H_2 + 2CO$ (0.14) 2CO (0.86)

[a] Neutral products for observed processes with branching ratios are listed.

Table 2

Reactions of Disubstituted n-butanes with Ions Derived from $Co(CO)_3NO$[a]

Reactant Neutral / Reactant Ion								
Co^+	$HF + H_2O$	(0.65)	$HCl + H_2O$	(0.59)	$HBr + H_2O$	(0.45)	$HBr + HCL$	(0.10)
	$H_2 + C_2H_5F$	(0.35)	$H_2 + C_2H_5Cl$	(0.35)	HBr	(0.21)	$CoCl$	(0.17)
			HCL	(0.06)	$H_2 + C_2H_5Br$	(0.25)	$CoBr$	(0.73)
					C_2H_5Br	(0.09)		
$CoCO^+$	HF	(0.06)	HCl	(0.19)	HBr	(0.09)	$HBr + HCl + CO$	(0.09)
	$HF + CO$	(0.18)	$HCl + CO$	(0.53)	$HBr + CO$	(0.71)	$HBr + CO$	(0.09)
	C_3H_5F	(0.09)	$HCl + H_2O + CO$	(0.13)	$HBr + H_2O + CO$	(0.13)	HBr	(0.06)
	$C_3H_5F + CO$	(0.67)	$C_3H_5Cl + CO$	(0.15)	$C_3H_5Br + CO$	(0.07)	$CoCl + CO$	(0.10)
							$CoBr + CO$	(0.66)
$Co(CO)_2{}^+$	$HF + CO$	(0.24)	$HCl + CO$	(0.77)	$HBr + CO$	(1.00)	$HBr + CO$	(0.59)
	$HF + 2CO$	(0.08)	$C_3H_5Cl + CO$	(0.23)			$HBr + 2CO$	(0.41)
	$C_3H_5F + CO$	(0.68)						
$CoNO^+$								
$CoCONO^+$	$HF + CO$	(0.27)			$HBr + CO$	(1.00)		
	$C_3H_5 + CO$	(0.73)						
$Co(CO)_2NO^+$	$HF + 2CO$	(0.34)	$HCl + 2CO$	(0.82)	$HBr + 2CO$	(1.00)	$2CO$	(1.00)
	$2CO$	(0.05)	$2CO$	(0.07)				
	$C_3H_5F + CO$	(0.21)	$C_3H_5Cl + CO$	(0.04)				
	$C_3H_5F + 2CO$	(0.40)	$C_3H_5Cl + 2CO$	(0.07)				
$Co(CO)_3NO^+$	$HF + 2CO$	(0.20)	$HCl + 2CO$	(0.45)	$HBr + 2CO$	(1.00)	$3CO$	(1.00)
	$C_3H_5F + CO$	(0.35)	$3CO$	(0.29)				
	$C_3H_5F + 2CO$	(0.45)	$C_3H_5Cl + 2CO$	(0.26)				

[a] Neutral products for observed processes with branching ratios are listed.

The simplest predicted structure of the product of the reaction is structure 4 as a result of HX loss from the intermediate shown.

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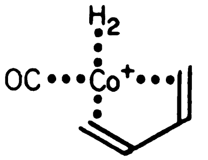

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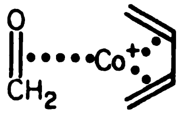


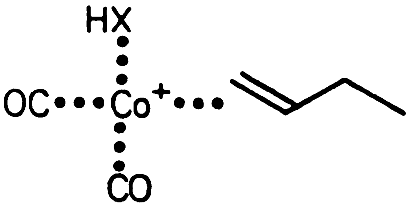
6

Structures 5 and 6 result from transfer of two H atoms from C_4H_8 to another part of the intermediate complex (i.e., two H atoms can migrate to the metal as an H_2 ligand or to the CO). Structure 5 is not acceptable since the H_2 would have been lost preferentially over the HX. Product 6 cannot be ruled out. Here, two H atoms are "stored" on the CO which has become CH_2O. Thermodynamically, this would be a favorable situation, since $PA(CH_2O) > PA(CO)$ by more than 25 kcal/mol. That is, transfer of two H atoms to CO produces a more strongly bound ligand. The chemistry of $CoCO^+$ with alkanes also suggests that H_2 may be "reversibly" stored on a CO ligand by forming CH_2O [77]. This would also explain why reaction (15) is not observed.

$$CoCO^+ + C_4H_9X \nrightarrow CoC_4H_9X^+ + CO \qquad (15)$$

Since the proton affinities of the hydrogen halides (HX) are similar to that for CO, CO loss and HX loss may be expected to be competitive processes. If, however, CO and C_4H_8 become H_2CO and C_4H_6 on the metal, only HX elimination would be expected.

The $Co(CO)_2^+$ ion reacts with the halobutanes to form the same products as $CoCO^+$ forms. An intermediate such as 7,



7

is reasonable since it does not violate the 18-electron rule and would predict that the weakly bound ligands are HX and CO. Since two CO's are not lost, a final product structure of 6, again, cannot be ruled out. Structure 6 may explain why $CoCO^+$ does not lose CO as a neutral, while $Co(CO)_2^+$ reacts only by losing one CO (never two). Again, the formation of butadiene may be the driving force leading to the conversion of CO to formaldehyde.

The $Co(CO)_xNO^+$ ions appear to react only by ligand substitution. There is no evidence that C_4H_9X is bound to the metal in the reaction products in any way except as the intact molecule. Note that the $Co(CO)_xNO^+$ ions do not react with fluorobutane. When $Co(CO)_xNO^+$ reacts with a haloalkane, an initial complex, $Co(CO)_xNO(XR)^+$, is formed. If the metal-RX interaction is strong, one or more CO's may be lost or a ligand decomposition may occur. Of the compounds studied, alkyl fluorides have the lowest PA's of the alkyl halides [78]. Thus, the initial metal-alkyl halide interaction should be least for X = F. The $PA(C_4H_9F)$ should be slightly greater than PA(CO), but this energy difference may not be large enough to overcome any activation barriers that lead to CO loss. (If this would ever be the case, it would occur for alkyl fluorides.)

In summary the results of Table 1 show that the $Co(CO)_x^+$ and $Co(CO)_xNO^+$ ions react with halobutanes to give products similar to those observed for other haloalkanes. The main difference between halobutanes and smaller haloalkanes which have been previously studied is that, when such a molecule contains a four-carbon chain, HX elimination can be followed by H_2 elimination to form a metal-butadiene complex.

B. Reactions of Cobalt-Containing Ions with 1-Bromo-4-Chlorobutane

The observed chemistry of the metal-containing species under study with this 1,4-dihalobutane parallels, in some respects, the halobutane reactions. Co^+ reacts by chloride and bromide abstraction but does not abstract both halogens simultaneously (in contrast to, e.g., 1,2-dihaloethanes). This is expected, since the formation of a diradical would accompany a $CoClBr^+$ product, which would not be thermodynamically possible. Apparently, interaction with the "Br end" of the molecule is favored over the "Cl end". Both homolytic and heterolytic cleavage of the C-Br bond is thermodynamically favored over the C-Cl bond (Table 3),so this behavior may be expected. Note that, when Co^+ reacts to form, e.g., CoCl, the resulting $C_4H_8Br^+$ could be a cyclic halonium ion. Again, Co^+ induces the formation of a metal-butadiene complex. Scheme I suggests possible differences in mechanism in the formation of butadiene from a 1,4-bisubstituted butane in contrast with a 1-halobutane. Scheme IB suggests that, if HBr elimination occurs, first, HCl loss may proceed in two ways. If the next step is formation of an allyl-type intermediate, a Cl shift must follow. While, β -halide shifts are typically not observed, allyl intermediates are commonly suggested [16]. Alternatively, insertion into C-Cl

Table 3

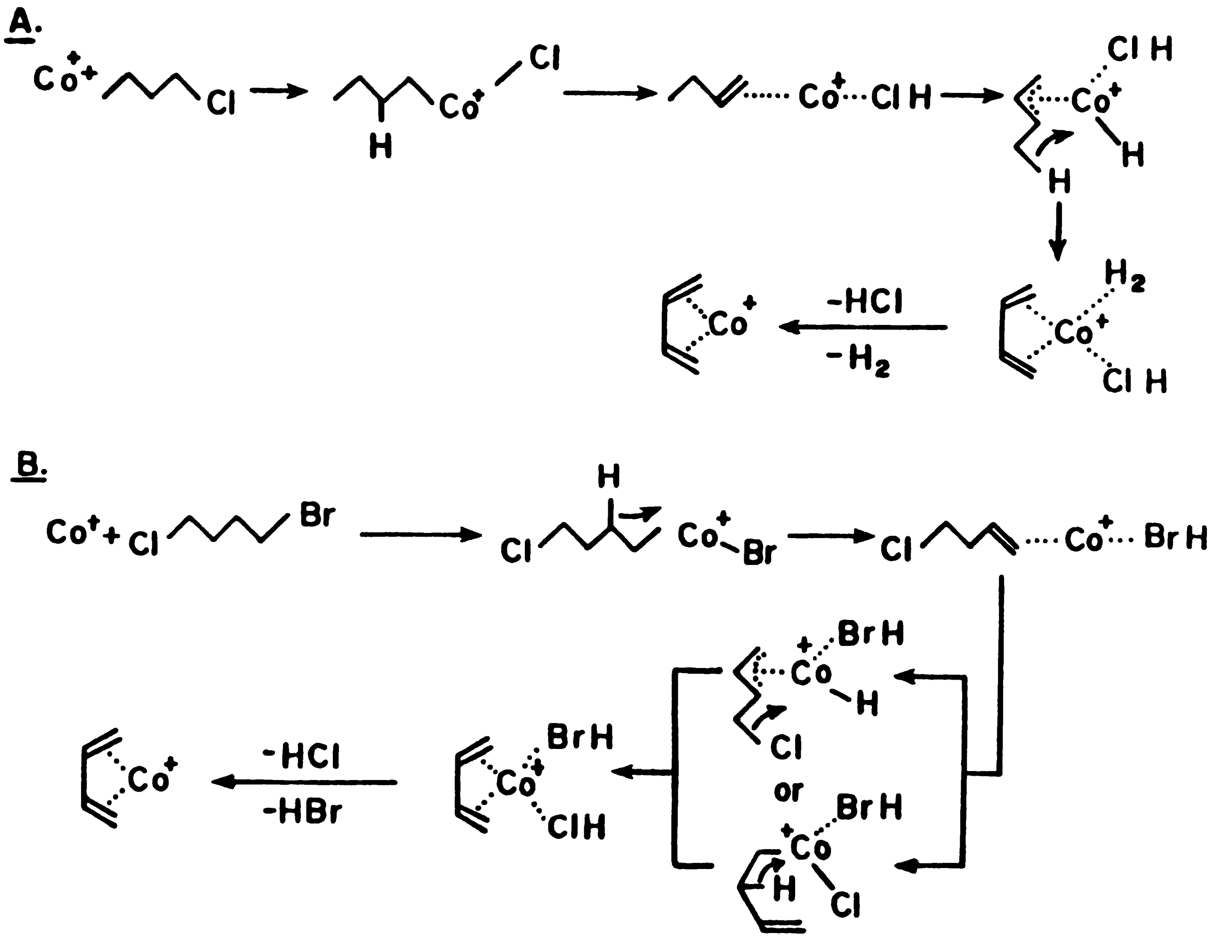
Rearrangement Energies[a]

Reaction		ΔH_{rxn} (kcal/mole)			
		X=F	OH	Cl	Br
$n\text{-}C_4H_9X$	$\rightarrow C_4H_9\cdot + X\cdot$	107.3	94.3	83.0	70.9
	$\rightarrow C_4H_8 + HX$	5.1	8.7	13.3	16.9
	$\rightarrow C_4H_6 + HX + H_2$	31.4	35.0	39.7	43.3
$HO(CH_2)_4X$	$\rightarrow \cdot C_4H_8X + OH\cdot$	90.1	--	90.1	90.1
	$\rightarrow \cdot C_4H_8OH + X\cdot$	102.8	--	78.0	63.7
	$\rightarrow C_4H_6 + H_2O + HX$	10.4	--	18.1	19.5
	$\rightarrow C_4H_7OH + HX$	5.1	--	12.8	14.2

$Cl(CH_2)_4Br \longrightarrow C_4H_6 + HCl + HBr$ $\quad \Delta H_{rxn} = 23.3$

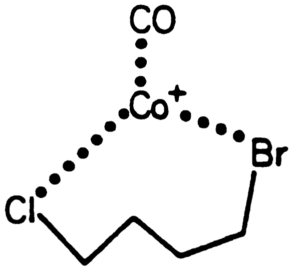
[a] Thermodynamic data was taken from references (79-81). In cases where heats of formation were not available, these were estimated using the group equivalence data in ref. (80).

Scheme I The Formation of Metal-Butadiene Complexes



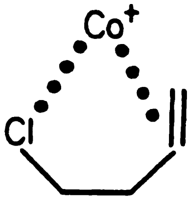
followed by a β-H shift may lead to HCl elimination.

The reactions of $CoCO^+$ also suggest that reaction at the "Br end" of this compound is favored over reaction at the "Cl end". Again, the formation of $CoC_4H_6^+$ is observed. The reactions of $CoCO^+$ may indicate that an initial interaction of both halogens with the metal may occur (structure **8**).



8

Presumably, the energy required to form CoCl from C_4H_9Cl and $CoCO^+$ is the same as with BrC_4H_6Cl as a reactant. Since the reaction only occurs for the dihalo compound, this may suggest the additional interaction between Co^+ and the "Br end" shown in **8**, that could provide additional energy in the complex to overcome any energy barrier. Since loss of { HCl + CO } is not observed as a process competitive with loss of {HBr + CO }, we assume that loss of {HBr + CO } implies a product with the structure **9**.



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Note that $CoCO^+$ loses CO in a number of reactions with bromochlorobutane. The loss of CO was not observed in reactions with the halobutanes. This may support the proposal that halobutanes react to form butadiene by "storing" H_2 on a CO (since there is no evidence suggesting a similar mechanism for bromochlorobutane leading to the formation of butadiene by "storing" HCl on a CO ligand).

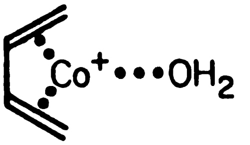
The $Co(CO)_2^+$ reactions also indicate preferential HBr elimination over HCl elimination.

Presumably, bromochlorobutane reacts with $Co(CO)_{2,3}NO^+$ by ligand substitution only. Since the bifunctional butane can displace three CO's, where the halobutanes displace only two CO's, multiple metal-ligand interactions of the type shown in $\underset{\sim}{8}$ are again suggested.

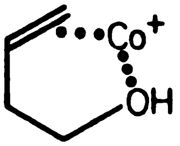
C. Reactions of Cobalt-Containing Ions with 1-Butanol

Fragmentation patterns following metal-induced rearrangements differ for butyl halides and butanol since H_2O and olefins have similar metal ion affinities (whereas hydrogen halides are much weaker in their interaction with metals than are olefins). Also, for many processes, alcohols are (thermodynamically) between chloroalkanes and fluoroalkanes (see Table 3). This, however, is not the trend for proton affinities. While PA information is not available for the halobutanes and butanol, data on the methyl and ethyl species indicate that the alcohols have much higher PA's than any of the halobutanes. This may explain the failure of Co^+ to form CoOH from butanol. The initial Co^+-organic interaction will be greatest for butanol. This energy may favor metal insertion instead of having insertion and abstraction compete, as is the case for haloalkanes. Note that Co^+ does not form CoOH in its reaction with ethanol (a primary alcohol), but it does with 2-propanol (a secondary alcohol) [19].

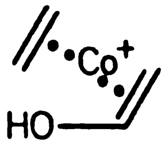
One way of explaining the products observed for 1-butanol is shown in Scheme II. Scheme II follows the assumption that the metal first rearranges butanol into butene and H_2O and that butene can then be induced to lose H_2. Thus, loss of H_2 as a neutral product implies that { C_4H_8O } on the metal is actually two ligands: (C_4H_6) and (H_2O). If H_2 elimination is observed, a number of ionic product complexes can be postulated (10-12).



10



11

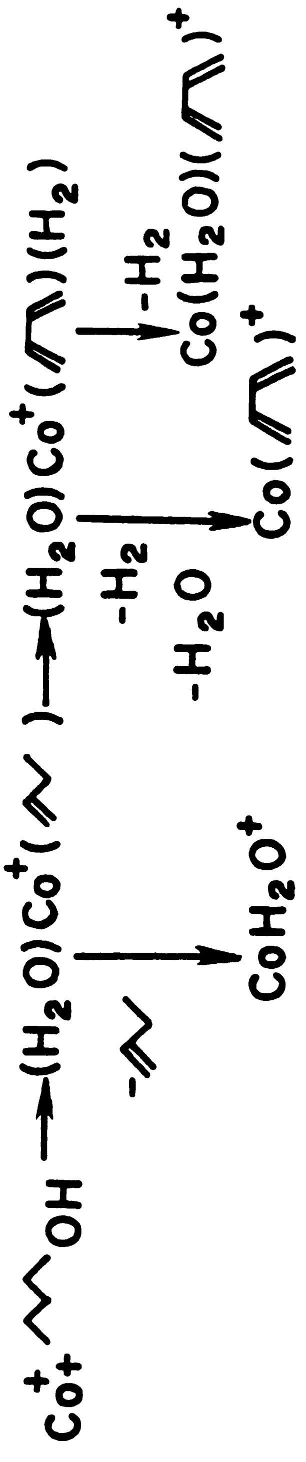


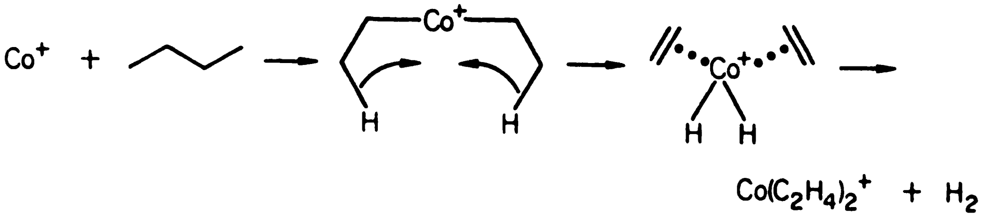
12

Complex 10 might be preferred since all studies of transition-metal ion reactions with alcohols give H_2O elimination. Thus, one might expect this to always be a first step. A second possible structure, 11 would only involve H_2 elimination forming a double bond between two skeletal atoms of butanol. There is some evidence in the literature that as the alkyl chain of monofunctional organic molecules increases, alkane-like chemistry is observed in addition to the reactions expected for that functional group [14,34,35]. Thus, we may expect the four-carbon chain to exhibit, to some extent, a chemistry typical for alkanes, such as reaction by H_2 elimination.

Recent work on alkanes suggests yet another mechanism for H_2 elimination. A fraction of the H_2 elimination in the reaction of Co^+ with n-butane appears to follow metal insertion into the central C-C bond [12]:

Scheme II





Such a mechanism would lead to the structure 12.

The reaction products of $CoCO^+$ could be explained by a mechanism very similar to Scheme II. With use of the proton affinity rule, the only unexpected process is the loss of C_4H_8, which should not be lost in the presence of a CO ligand.

Table 4 lists CID results for two ions that were products of $CoCO^+$ reaction with butanol. The CID spectrum of $CoC_4H_{10}O^+$ implies that it exists as a mixture of $Co(C_4H_8)(H_2O)^+$ (which would have as CID products, m/z 77, 115, and 113) and $Co(C_2H_4)(C_2H_5OH)^+$ (which would form m/z 87 and 105 as CID products). The major CID product of $CoCOC_4H_8O^+$ is $CoC_4H_8O^+$, implying that H_2 elimination occurs leaving the molecular skeleton intact, i.e., the structure is similar to 11. The CID products at m/z 87 and 103 may be CIR products of a species similar to 11 since the following reactions have been observed for 3-buten-1-ol [34,35] with Co^+:

Table 4

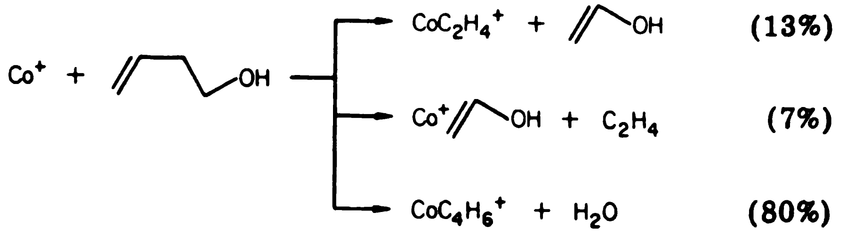
CID Results/Ionic Products of $CoCO^+$ with Butanol

$$CoCO^+ + n\text{-}C_4H_9OH \longrightarrow CoC_4H_{10}O^+ \ (m/z\ 133) + CO$$

$$CoCO^+ + n\text{-}C_4H_9OH \longrightarrow CoCOC_4H_8O^+ \ (m/z\ 159) + H_2$$

-------- CID Products of 133 ----------		
m/z	R.I.	Assignment
59	69.4	Co^+
77	34.7	CoH_2O^+
87	100	$CoC_2H_4^+$
105	39.8	$CoCOH_2O^+$ and/or $CoC_2H_5OH^+$
113	19.8	$CoC_4H_6^+$
115	38.7	$CoC_4H_8^+$
131	29.8	$CoC_4H_8O^+$

------ CID Products of 159 ------		
m/z	R.I.	Assignment
59	10.2	Co^+
87	22.5	$CoCO^+$ and/or $CoC_2H_4^+$
103	5.1	$CoC_2H_3OH^+$
131	100	$CoC_4H_8O^+$



That is, evidence suggests that structures 10, 11, and 12 are formed during H_2 elimination. If 12 is a contributing structure, loss of "C_4H_8" (56 u) may, instead, be loss of { CO and C_2H_4}. This possibility is consistent with the PA rule.

The formation of $CoNOH_2O^+$ in the reaction of $CoNO^+$ with 1-butanol parallels smaller alcohol reactions with this ion. Selective retention of H_2O over olefins is consistently observed [19] for $CoNO^+$. The same is observed for $CoCONO^+$.

The reactions observed for $Co(CO)_{2,3}NO^+$ cannot go through intermediates with all ligands bound to the metal. Therefore, reactions must proceed through a series of ligand losses and metal-induced reactions and intermediates such as $Co(CO)_3NO(C_4H_8O)(H_2)^+$ would not be expected.

CID results on some products of $Co(CO)_{2,3}NO^+$ reactions are listed in Table 5. The CID spectra of m/z 163 and 191 imply that $C_4H_{10}O$ exists on the metal predominately as {C_4H_8 and H_2O}. Also, the CID spectrum of the product of m/z 189 suggests that H_2 loss occurs leaving a structure similar to 11.

Thus, in light of the reported chemistry of alcohols with CoL_x^+ to date, 1-butanol is surprising in its reactivity. The high PA of alcohols suggests a strong initial metal-alcohol interaction. That is, in the formation of the complex

Table 5

CID Results/Ionic Products of $Co(CO)_{2,3}NO^+$ with Butanol

$$\mathrm{CO(CO)_3NO^+ + n\text{-}C_4H_9OH} \rightarrow \mathrm{CoCONOC_4H_8O^+}\ (m/z\ 189) + 2CO + H_2$$

$$\mathrm{CO(CO)_3NO^+ + n\text{-}C_4H_9OH} \rightarrow \mathrm{CoCONO(C_4H_{10}O)^+}\ (m/z\ 191) + 2H_2$$

---- CID Products of 189 ----

m/z	R.I.	Assignment
87	11.2	$CoCO^+$
89	9.1	$CoNO^+$
161	100	CoNO( OH)$^+$

--------- CID Products of 191 ---------

m/z	R.I.	Assignment
57	12.4	$C_4H_9^+$
107	39.3	$CoNOH_2O^+$
115	2.3	$CoC_4H_8^+$
145	12.0	$CoNOC_4H_8^+$
161	1.5	$CoNOC_4H_8O^+$ (possibly $CoNO(C_4H_6)(H_2O)^+$
163	100	$CoNOC_4H_{10}O^+$

$$\mathrm{Co(CO)_2NO^+ + n\text{-}C_4H_9OH} \rightarrow \mathrm{CoNOC_4H_9OH^+}\ (m/z\ 163) + 2CO$$

--- CID Products of 163 ----

m/z	R.I.	Assignment
41	8.2	$C_3H_5^+$
57	50.4	$C_4H_9^+$
89	37.3	$CoNO^+$
107	100	$CoNOH_2O^+$
115	19.7	$CoC_4H_8^+$
135	2.4	$CoNOC_2H_6O^+$
145	25.5	$CoNOC_4H_8^+$

$[CoLx(RX)^+]^*$, a relatively large amount of energy is available in the complex when X = OH. This energy may promote this rich chemistry. CID results are useful in attempting to make structural assignments for product ions.

D. Reactions of Cobalt-Containing Ions with 4-Halo-1-butanols

In light of the results for the halobutanes, butanol, and chlorobromobutane, the halobutanols exhibit an unexpected chemistry. Insertion into C-C bonds becomes a major mechanistic step in many cases.

Again, the formation of Co^+-butadiene is observed. Table 6 indicates the CID spectrum of a $CoC_4H_6^+$ product with no evidence for any structure except a simple metal-alkadiene complex.

In the formation of Co^+-butadiene, dehydration and dehydrohalogenation occur. The data in Table 2 suggest that dehydrohalogenation may occur first, since it can occur without subsequent dehydration. Consider the reaction of $Co(CO)_3NO^+$ with bromobutanol by loss of { HBr + 2CO }:

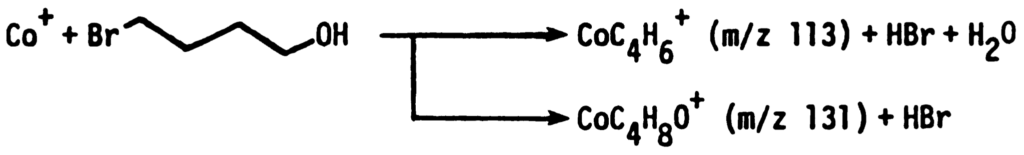
$$Co(CO)_3NO^+ + BrC_4H_8OH \xrightarrow{\qquad\qquad} CoCONO(C_4H_8O)^+ + 2CO + HBr$$

The C_4H_8O must exist intact on the metal, since other possibilities such as the combination of ligands {C_4H_6 and H_2O } would violate the 18-electron rule. Thus, HBr elimination was induced but not H_2O elimination.

Co^+ reacts with chloro- and bromobutanol by eliminating HX. Again, similar to the assignment problem in butanol alone, a number of product structures could be suggested (10, 11, 12). The CID data in Table 6 may be interpreted as evidence for a mixture of all three structures plus possibly a fourth; 13. The most surprising reaction of Co^+

Table 6

CID Results/Ionic Products from Reactions of Co^+ with 4-Bromo-1-Butanol

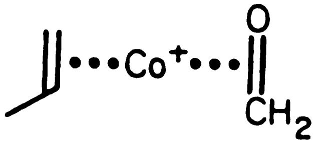


--- CID Products of 113 ----

m/z	R.I.	Assignment
59	100	Co^+

--- CID Products of 131 ----

m/z	R.I.	Assignment
113	100	$CoC_4H_6^+$
103	13.1	$CoC_2H_3OH^+$
101	29.0	$CoC_3H_6^+$
89	4.0	$CoCH_2O^+$
87	1.0	$CoC_2H_4^+$
71	41.4	$C_4H_7O^+$
59	50.5	Co^+



13

is the elimination of {C_2H_5X + H_2} from the three halobutanols. Note that a similar pathway was not observed for the monofunctional compounds or the dihalobutane. Apparently, both functional groups (one being an OH) contribute to an intermediate geometry favoring attack of the central C-C bond, presumably following the mechanism shown in Scheme III.

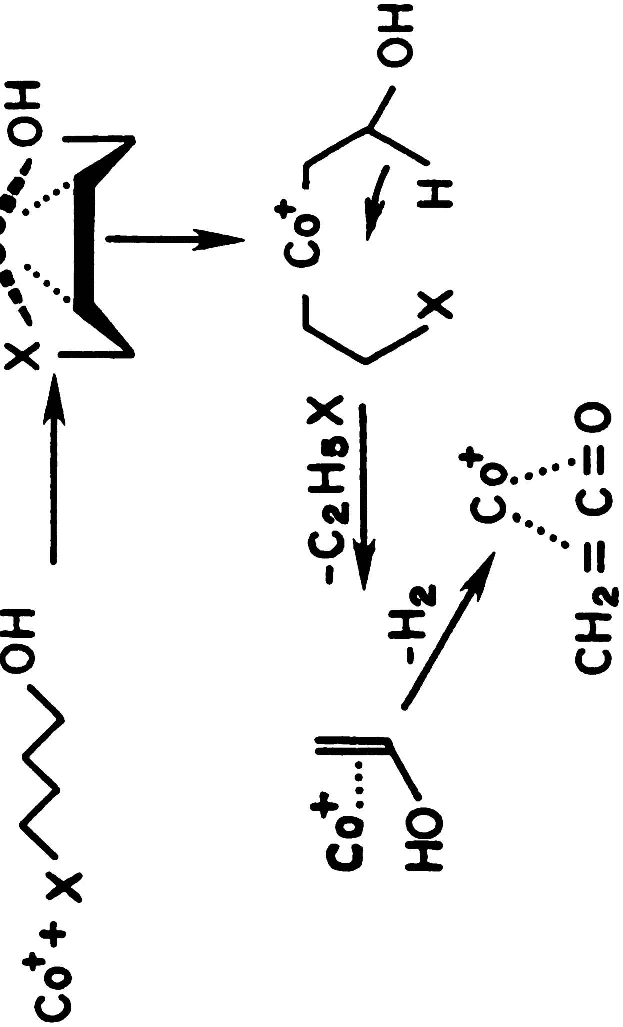
Transition metal ion/ketene complexes have been previously observed as reaction products [3,13]. Failure to see the intermediate Co^+-allyl alcohol complex is, however, surprising.

The $CoCO^+$ ion reacts to form a metal-methanol complex. Note that (a) loss of C_3H_5X does not occur with Co^+ or $CoNO^+$ as a reactant, (b) the process only occurs with CO's present on the metal, (c) one CO is always lost, and (d) the process only occurs for the bifunctional compounds, where one group is an alcohol.

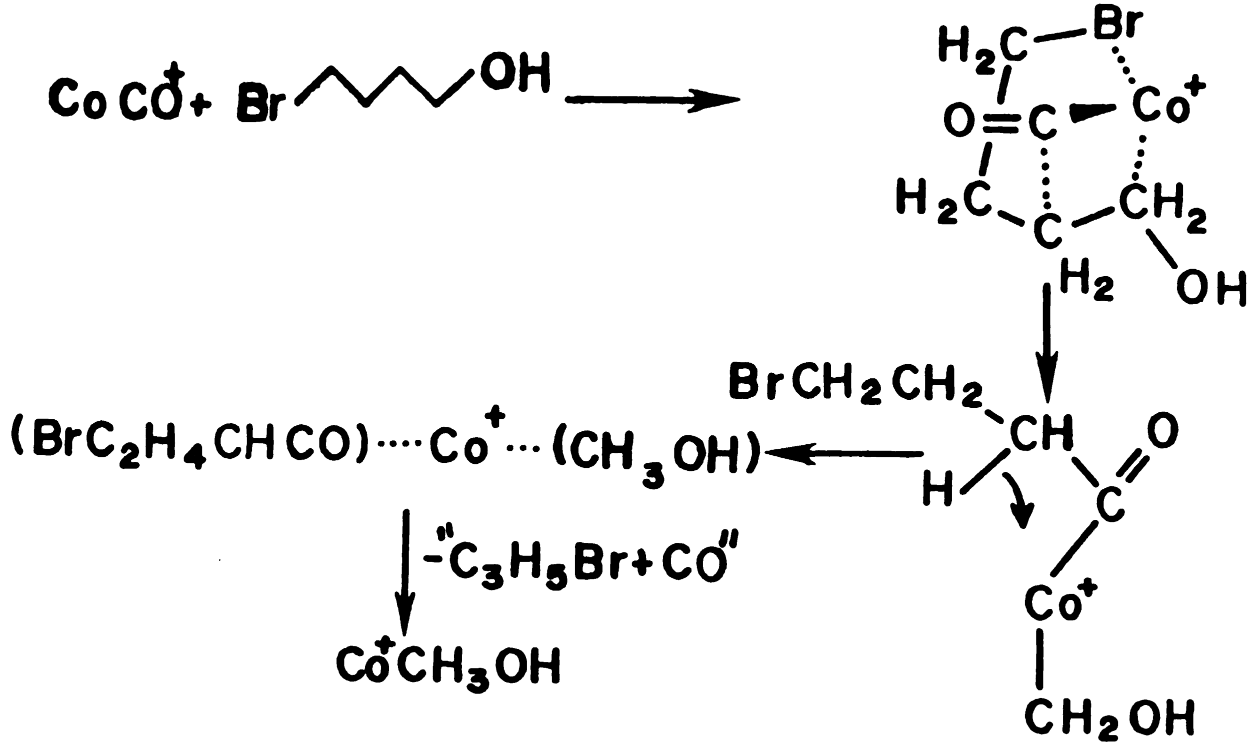
These observations suggest a mechanism involving insertion of the CoCO groups into a C-C bond followed by a β-H shift, leaving a methanol complex. A possible mechanism is given in Scheme IV. The implication in the scheme is that the initial complex is of a geometry such that attack of the C-C(OH) bond is favored [82].

Table 2 shows that the mechanism in Scheme IV occurs for fluoro- and chlorobutanol, with $CoCO^+$, $Co(CO)_2{}^+$, and $Co(CO)_{2,3}NO^+$. In contrast, the reaction only occurs for bromobutanol with $CoCO^+$. Since the C-X bond is

Scheme III



Scheme IV


Co CO$^+$ + Br
OH
H$_2$C
Br
O=C
Co$^+$
H$_2$C
C
CH$_2$
H$_2$
OH
BrCH$_2$CH$_2$
CH
O
C
H
Co$^+$
CH$_2$OH
(BrC$_2$H$_4$CHCO)····Co$^+$···(CH$_3$OH)
-"C$_3$H$_5$Br+CO"
Co$^+$CH$_3$OH

weakest for X = Br (of the series of halogens studied), metal insertion leading to HBr elimination may occur much more readily than insertion into C-C bonds.

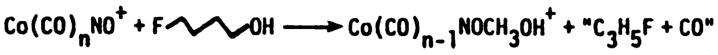
The $Co(CO)_xNO^+$ reactions with the halobutanols are fairly straightforward. Note that, while monofunctional compounds appear to react with the $Co(CO)_xNO^+$ ions predominately by ligand displacement, bifunctional molecules exhibit a rich chemistry with these ions. A number of product ions of the type $Co(CO)_xCH_3OH^+$ and $CoNO(CO)_xCH_3OH^+$ from reactions of fluorobutanol were analyzed by collision induced dissociation. The results are given in Table 7. These results imply simple complexes containing methanol intact.

Table 7

CID Results/Products of Reactions with Fluorobutanol

---- CID Products of 119 ----

m/z	R.I.	Assignment
91	39.4	$CoCH_3OH^+$
87	100	$CoCO^+$
59	44.8	Co^+



n = 1, m/z = 121
n = 2, m/z = 149
n = 3, m/z = 177

- CID Products of 121 --

m/z	R.I.	Assignment
91	9.1	$CoCH_3OH^+$
89	100	$CoNO^+$
59	29.0	Co^+

- CID Products of 149 --

m/z	R.I.	Assignment
121	18.4	$CoNOCH_3OH^+$
119	1.5	$CoCOCH_3OH^+$
117	1.3	$CoCONO^+$
91	8.2	$CoCH_3OH^+$
89	100	$CoNO^+$
59	19.4	Co^+

- CID Products of 177--

m/z	R.I.	Assignment
121	53.7	$CoNOCH_3OH^+$
117	8.1	$CoCONO^+$
91	9.3	$CoCH_3OH^+$
89	100	$CoNO^+$
59	13.4	Co^+

CHAPTER 4

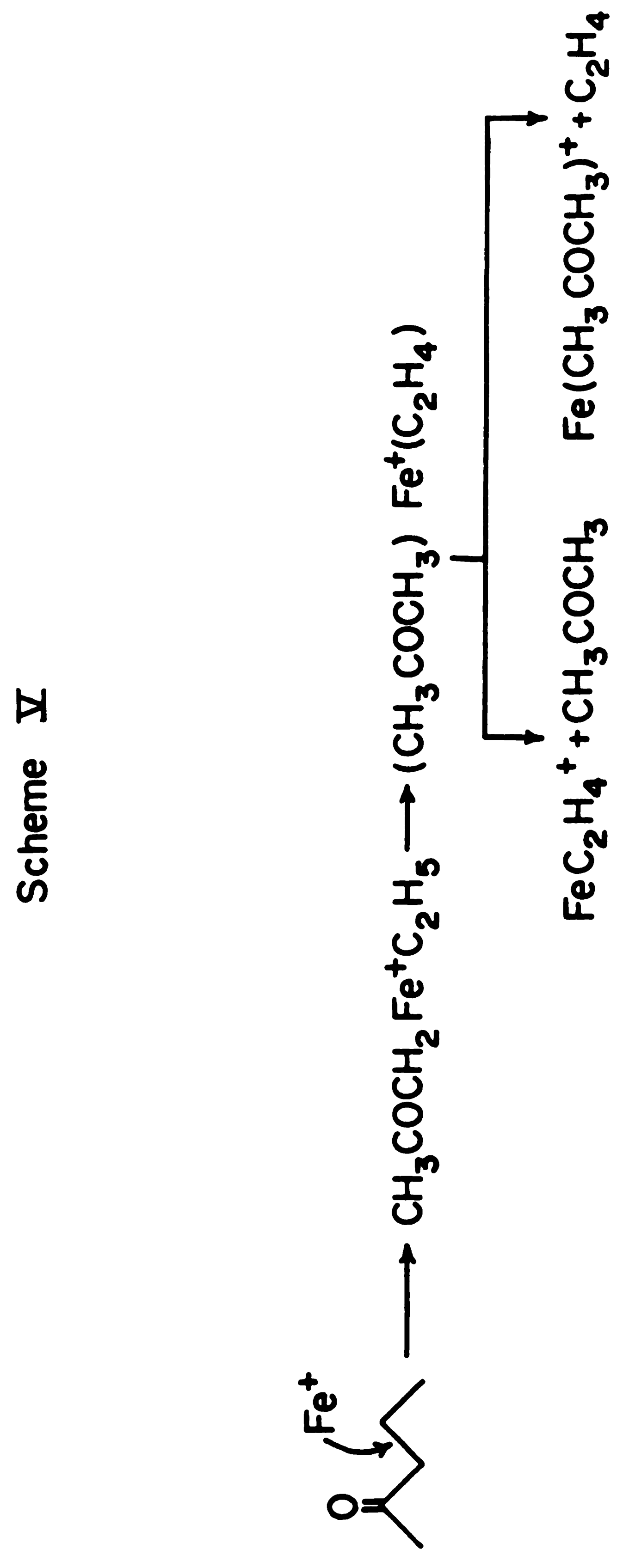
THE CHEMISTRY OF COBALT-CONTAINING IONS WITH A SERIES OF 1-CHLORO- AND 1-HYDROXY-n-ALKANES

I. Current Understanding of the Mechanistic Sequence

Based on the discussion in the preceding chapter, one may expect an ion such as Co^+ to dehydrate all alcohols. In the case of n-butanol (Table 1), this was observed, however insertion into C-C bonds also occurs. In other words, n-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 [3] (Scheme V). Also, in the case of nitroalkanes [26], 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.

Therefore, basic questions concerning the metal insertion/β-H shift/competitive ligand loss mechanistic sequence and especially the metal insertion step, which appears to be the least understood step, need to be

Scheme V



Fe+
CH3COCH2Fe+C2H5
(CH3COCH3) Fe+(C2H4)
FeC2H4+ + CH3COCH3
Fe(CH3COCH3)+ + C2H4

answered.

In this work, the gas phase chemistry of Co^+ with a series of 1-chloro- and 1-hydroxy-n-alkanes with the alkyl chain varying from three to eight carbon atoms is presented. The results of these experiments are listed in Tables 8 and 9, along with those of the corresponding alkanes for comparison. These chain length studies can answer questions such as, why Co^+ does *not* insert into the C-C bond in ethanol or i-propanol, but does in n-butanol; and why Co^+ *only* inserts into the C-Cl bond in ethyl, n-propyl and n-butyl chlorides.

Our long range goal is to sufficiently understand all three steps of the mechanistic sequence, which will lead to a more accurate prediction of the branching ratios for bimolecular organometallic reactions, which is especially important for metal ion chemical ionization mass spectrometric analysis.

Our current level of understanding of the three mechanistic steps will be discussed in the context of alkane reactions. The three steps, metal ion insertion, β-H shift, and competitive ligand loss will be considered separately.

The 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 [83]:

$$Co^+ + CH_3CH_2CH_2CH_3 \rightarrow \left\{ \begin{array}{llr} \rightarrow CoC_4H_8^+ + H_2 & (39\%) & (16) \\ \rightarrow CoC_3H_6^+ + CH_4 & (\ 9\%) & (17) \\ \rightarrow CoC_2H_4^+ + C_2H_6 & (52\%) & (18) \end{array} \right.$$

Table 8

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

[a] H_2 elimination is listed under HX elimination for X = H

[b] Reference 83

Table 9

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

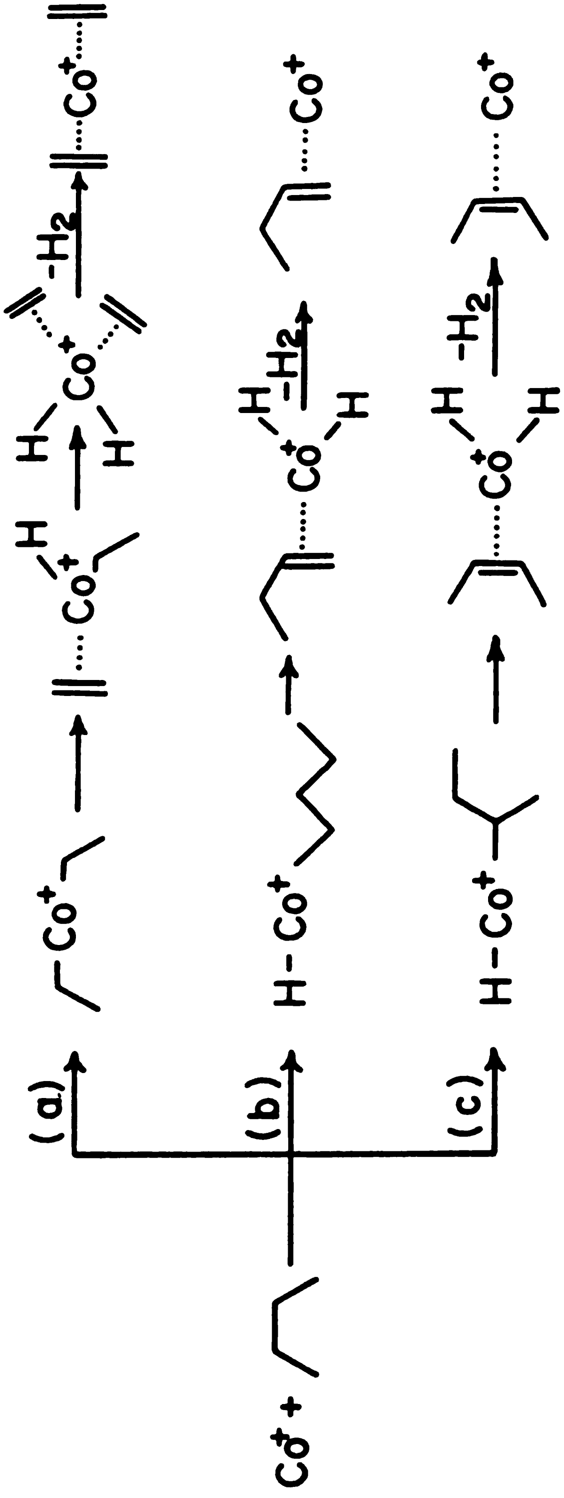
[b] Reference 83

Based on the above distribution and the accepted mechanism, we might conclude that Co^+ inserts into the internal C-C bond most often (leading to the products in (18)), with C-H insertion of "second priority", (reaction 16), and insertion into the terminal C-C bond (reaction 17) 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 [84]. 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 VI,a). Labelling studies suggest that Co^+ dehydrogenates n-butane by both 1,2- and 1,4-elimination processes (Scheme VI) [12]. These studies suggest that Co^+ dehydrogenates butane 51% via Scheme VIa and 49% via Co^+ insertion into C-H bonds, Scheme VIb,c (if the products are interpreted neglecting the possibility of scrambling); however, this distribution may also reflect isotope effects. Freiser et al. [30] suggest that the mechanism in VIa 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.

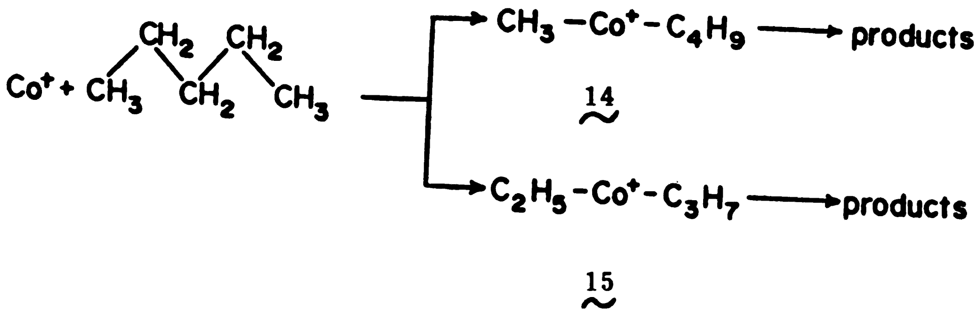
With this information, i.e., since 90% of the process in reaction (16) follows from the same insertion intermediate involved in reaction (18), the branching ratios would then suggest that 87% of the reaction products in the Co^+-butane system are due to insertion into the internal C-C bond, 9% are due 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 [83] have interpreted the reaction products for Co^+ with n-alkanes, to obtain the order of preference for transition metal ion

Scheme VII



insertion into skeletal bonds. They point out a correlation between the possibility 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. The two different skeletal bonds into which metal insertion may occur are shown below.

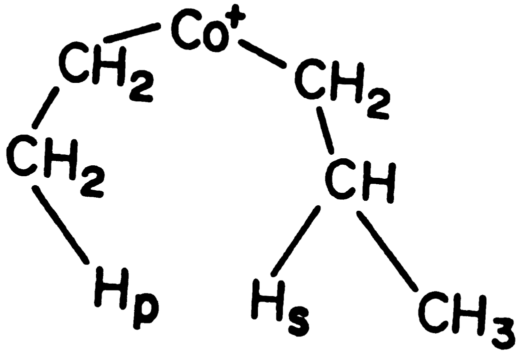


A larger fraction of the products appear to be formed via intermediate 15 than 14. Also, note that $\{IP(CH_3\cdot) + IP(C_4H_9\cdot)\} > \{IP(C_2H_5\cdot) + IP(C_3H_7\cdot)\}$. It has been proposed that this correlation exists because IP(R·) reflects the polarizability of (R·), and the bond strength $D°(Co^+\text{-}R)$ increases as the polarizability of (R·) increases [12,83].

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 $R\text{-}Co^+\text{-}R'$ 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 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.

The 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, based on the preferred reaction site. 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 15. As redrawn (16), the two accessible β-H's are H_p and H_s.



16

The fact that C_2H_6 elimination is a more prominant 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^+ [11].

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

The Competitive Ligand Loss Step. Of the three mechanistic steps, this last step has been characterized most completely, as it was seen in the previous chapter. In almost all cases, when the complex $M^+(A)(B)$ dissociates, the ligand with the lower proton affinity (PA) is preferentially lost ("PA Rule" - Chapter 3). For example, in the reaction of Fe^+ with 2-pentanone [3], Scheme V, insertion into a C-C bond leads to the complex $(CH_3COCH_3)Fe^+(C_2H_4)$. Since acetone is the better base in the gas phase ($PA(CH_3COCH_3) > PA(C_2H_4)$), it is expected that the retention of acetone will be a dominant process; this is consistent with the experimental results. This "PA Rule" appears to always hold in the reactions of Co^+ with alkanes, and all of the reactions presented in this work.

In this work, an attempt is made to interpret the products of Co^+ with 1-chloro-n-alkanes and n-alcohols in order to suggest an ordering for preferred site of attack of skeletal bonds. These orders of preference will be compared with those of the corresponding alkanes to demonstrate the effects due to the functional group. Along with the insights into the metal insertion step, some insights into the β-H shift process can be provided by these studies. Trends in β-H shifts will be discussed and will be compared and contrasted with those observed for the corresponding alkanes.

II. Insights Into the β-H Shift Process

Some interesting insights into the β-H shift process can be provided from these chain length studies. The implications of the β-H shift trends are presented first, since they are pertinent to the data interpretation that follows.

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

$$R-Co^{+}-R'$$

where both R- and R' have β-H atoms that can shift. In the case of intermediate **16**, Halle, Armentrout and Beauchamp [11] first pointed out the shift of a secondary β-H is preferred over that of a primary β-H; thus, more $CoC_3H_6^+$ results from **16** than $CoC_2H_4^+$. This is also the case for the Fe^+ and Ni^+ analogs to **16**.

A similar analysis of the data in Table 8 and 9 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. The shorthand notation β-H $(n\text{-}C_3) >$ β-H (C_2) will be used. 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 a β-H (n-C_3) > β-H (n-C_5). Beauchamp's results for Co^+ and octane show the expected order [84], with the β-H (C_5) shift being slightly favored over the β-H (C_3) shift.

The results of Radecki and Allison [83] 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

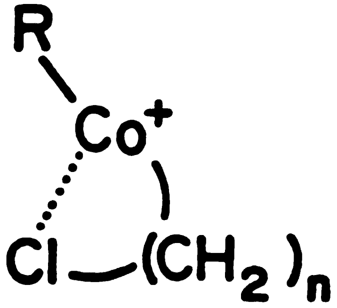
$$\beta\text{-H}(C_2H_5) < \beta\text{-H}(n\text{-}C_3H_7) < \beta\text{-H}(n\text{-}C_4H_9)$$

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 $-CH_2-CH_2Cl$ the same as that for $-CH_2CH_3$? Consider as an example, the products for n-chlorooctane resulting from the intermediate

$$C_3H_7\text{-}Co^+\text{-}(CH_2)_5Cl$$

The results in Table 9 suggest that only the β-H from the n-C_3H_7- group shifts. In fact, an analysis of the chloroalkane results in Tables 8 and 9 reveals that a β-H shift from a chloroalkyl group <u>never</u> occurs. We conclude that this is a kinetic effect. A subsequent metal-halogen interaction following Co^+ insertion into various C-C bonds



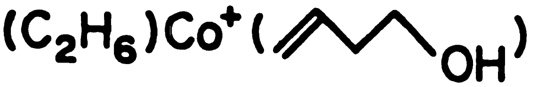
moves the β-H of the chloroalkyl group away from the metal making it inaccessible. This explanation has been used previously to explain the failure of a β-H shift to occur [26].

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

$$C_3H_7\text{-}Co^+\text{-}C_2H_4OH$$

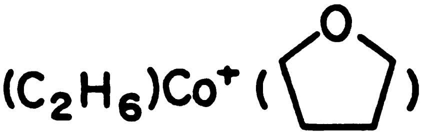
is apparently formed. <u>No</u> products resulting from a β-H shift from the hydroxy-ethyl group are observed. There are instances where H-shifts from

$-(CH_2)_2OH$ 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 <u>one</u> hydroxy-alkyl group for which a H-shift consistently occurs preferentially over whatever alkyl group is present; this is the $-(CH_2)_4$-OH 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 VII for hexanol. 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 $-(CH_2)_4$-Cl is not observed. Since it is not a β-H shift, the intermediate formed in Scheme VII is probably not (17)



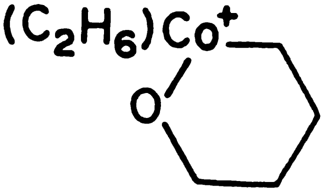
17

but contains either tetrahydrofuran (THF) (18)



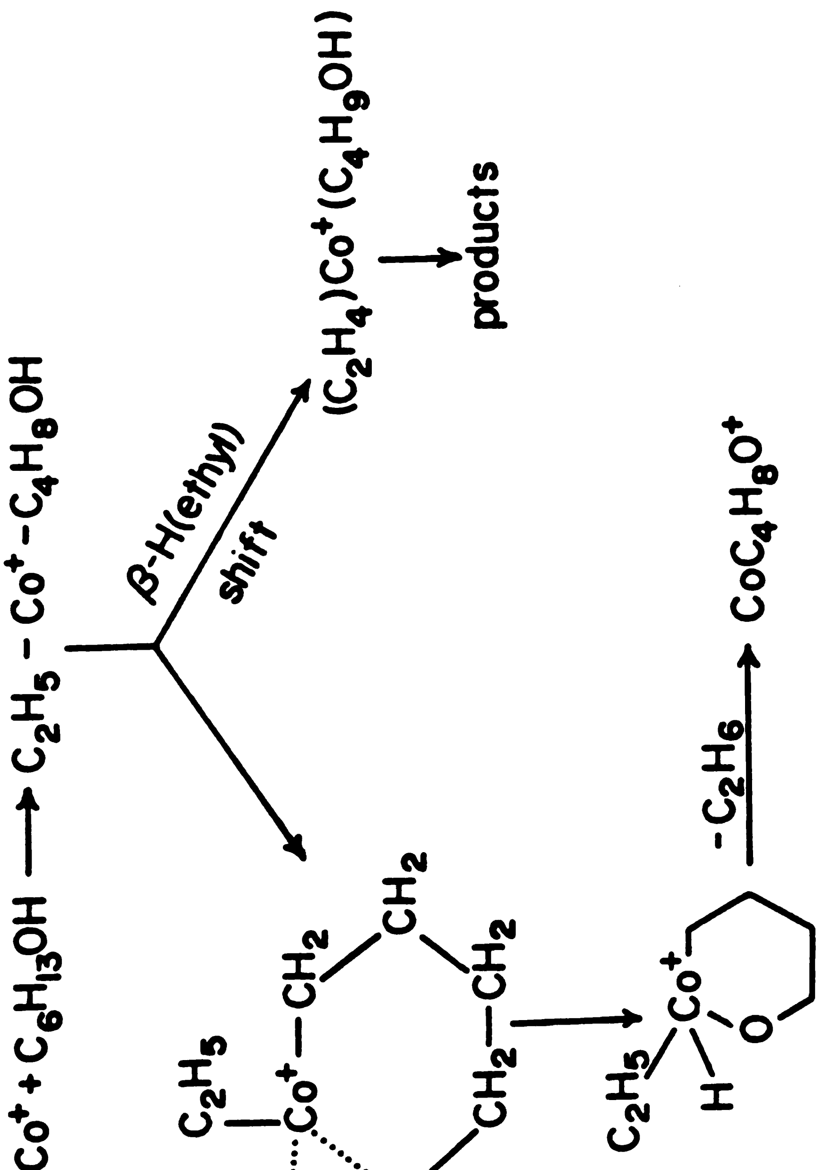
18

or a metallacycle (19)



19

Scheme VII



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 8 and 9. 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 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 hydroxylalkyl groups appears to be the hydroxy-hydrogen atom, and most likely from the $-(CH_2)_4$-OH group, H_2 elimination for alcohols must be predominantly a 1,7-elimination. Using n-octanol as an example, Scheme VIII shows the H_2 elimination following insertion into the C_4H_9-C_4H_8OH bond.

Similarly we suggest that H_2 elimination from n-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.

III. Insights into the Metal Insertion Step/Order of Preference for the Metal Insertion

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 10 follows the discussion of alkane chemistry at the beginning of this chapter, and has been also discussed elsewhere [83]. Note that the experimental results in Tables 8 and 9, do not suggest a random or nonselective mode of

Scheme VIII

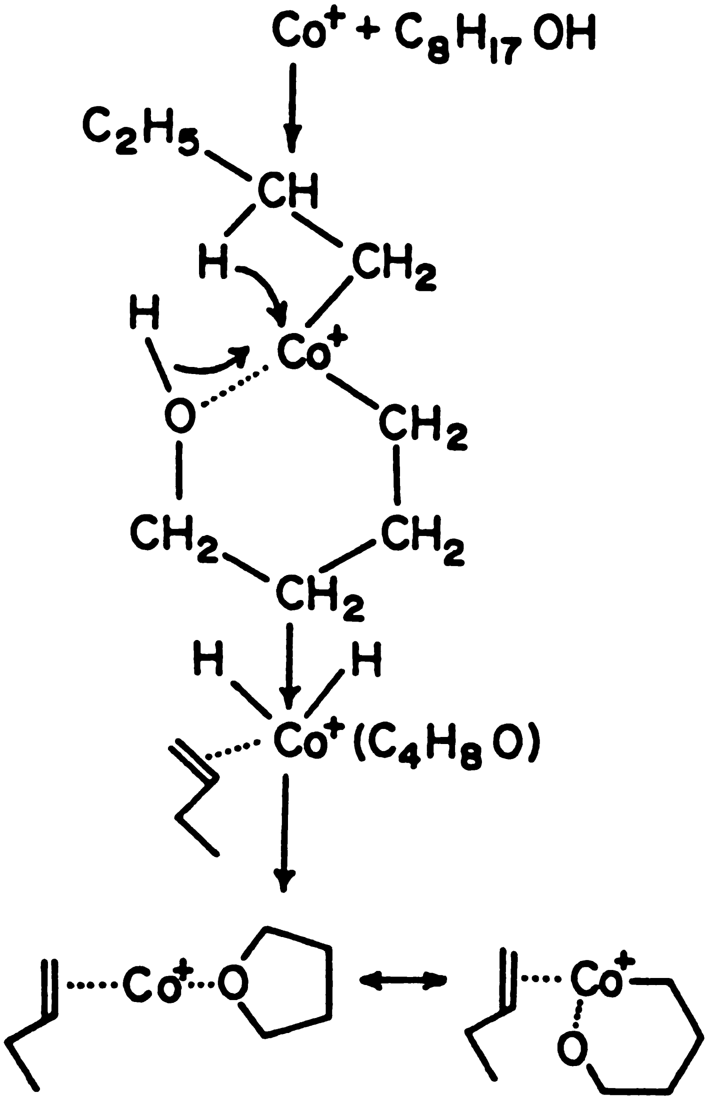
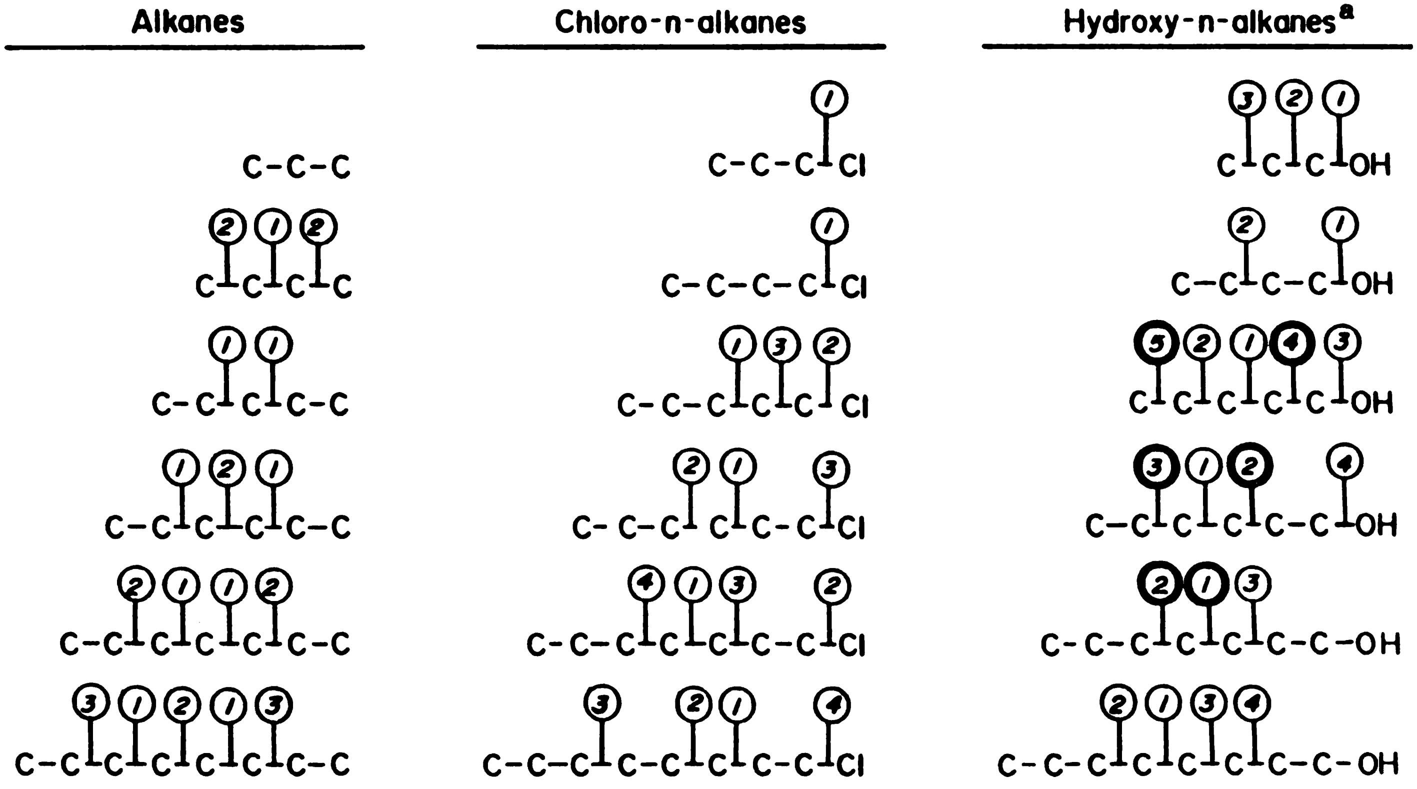

Co+ + C8H17OH
C2H5
CH
H
CH2
H
Co+
O
CH2
CH2
CH2
CH2
H
H
Co+(C4H8O)
Co+
O
Co+
O

Table 10

Order of Preference for the Metal Insertion



[a] The ordering of bond insertion preference for alcohols shown here assumes that the $Co(C_4H_6)^+$ 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.

insertion that assumes every C-C bond is equally susceptible to attack. In Table 10, 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.

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 10, consider the case of n-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 due 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 [34,35]. 26% of the reaction products of Co^+ with THF are $CoC_4H_6{}^+$ [20]. 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%) [16]. Since $CoC_4H_6{}^+$ is formed in the chloroalkanes, and based on the β-H shift discussion, the trends in Table 10 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 n-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. Twenty-five percent 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:

$$C^3\text{-}C^4 > C^4\text{-}C^5 > C^1\text{-}OH > C^2\text{-}C^3$$

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

$$C^4\text{-}C^5 > C^3\text{-}C^4 > C^1\text{-}OH > C^2\text{-}C^3$$

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 8 and 9, 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 10.

IV. The Chemistry of Co^+ with 1-Chloro-n-Alkanes

Reactions (2)-(4) (Chapter 3) are typical for small alkyl halides. The results for 1-chloropropane in Table 8 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

$$RX + Co^+ \longrightarrow R^+ + CoX \tag{19}$$

is only observed for the chloroalkanes in Tables 8 and 9. In the case of R = C_3H_7, reaction (19) is only exothermic 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 [85], and the Co^0-Cl

[86] bond is stronger than the Co^0-CH_3 [88] and Co^0-H [88] bonds, and possibly the Co^0-OH [89] 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:

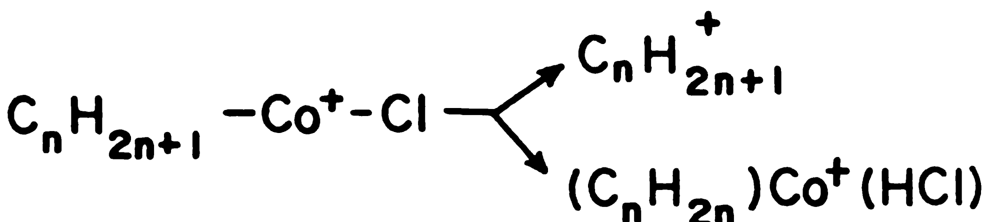


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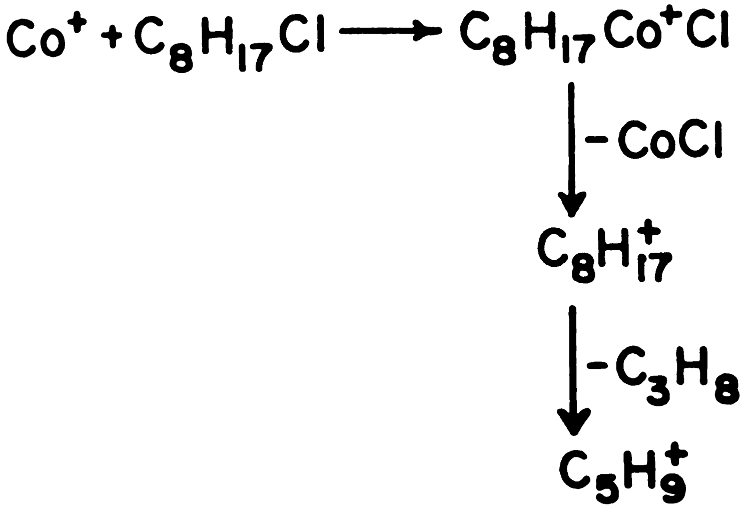
Table 8 and 9 show that, as n increases, intermediate 20 tends to dissociate to $C_nH_{2n+1}^+$, rather than undergo the β-H shift. This is expected since the alkyl ion formation becomes increasingly exothermic, since IP(C_nH_{2n+1}) decreases with increasing n. Because of this, $Co(HCl)^+$ and $Co(C_nH_{2n})^+$ products are not observed for the larger chloroalkanes in Tables 8 and 9.

While we expect reaction (19) 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-$C_5H_9^+$ [90]. Thus, failure to observe $C_8H_{17}^+$ may be due to rapid fragmentation following its formation as in reaction (20).



$$\begin{tikzcd}
Co^{+} + C_8H_{17}Cl \arrow[r] & C_8H_{17}Co^{+}Cl \arrow[d, "-CoCl"] \\
 & C_8H_{17}^{+} \arrow[d, "-C_3H_8"] \\
 & C_5H_9^{+}
\end{tikzcd} \qquad (20)$$

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.

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 process parallel reaction (19). For intermediates of the type

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

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

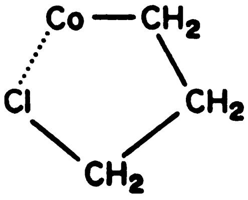
1-chloro-n-pentane and 1-chloro-n-hexane; $C_4H_9^+$ is formed from 1-chloro-n-hexane and 1-chloro-n-heptane, etc. Similar products are reported in endothermic reactions of Co^+ with alkanes [9]. Again, the presence of the -Cl group makes this process exothermic for the larger R-X, only where X = Cl. Consider the reaction

$$Co^+ + n\text{-}C_7H_{15}Cl \longrightarrow C_4H_9^+ + \text{"}CoC_3H_6Cl\text{"} \tag{21}$$

The possible neutral products may be:

$CoCl + C_3H_6$

21



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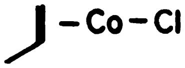


23

The reported products cannot be CoCl and propene, 21, since the overall reaction would be endothermic by approximately 12 kcal/mol. Since $D^0(Co^0\text{-}CH_3) = 41 \pm 10$ kcal/mol [88] and $D^0(Co^0\text{-}Cl) = 92.8 \pm 1.9$ kcal/mol [86], we prefer structure 23 over 22. Reaction (21) would be exothermic if the metal product was 23, and if $D^0(ClCo^0\text{-}C_3H_6) > 10.8$ kcal/mol, which would not be unlikely. If the Co-Cl interaction in intermediate 22 were sufficient to make (21) exothermic, we would also expect to observe the analogous reaction for n-heptanol. Since we do not observe this, and since D(R-Cl) < D(R-OH) [85], we suggest that reaction (21) occurs via Co^+ insertion into the $C_4H_9\text{-}C_3H_6Cl$

bond, and, as charge transfer occurs to form $C_4H_9^+$, the CoC_3H_6Cl, 22, rearranges to, 23, prior to fragmentation.

In light of this discussion, we note that reaction (22)

$$Co^+ + n\text{-}C_7H_{15}Cl \longrightarrow C_5H_9^+ + \{CoCl + C_2H_6\} \qquad (22)$$

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 8 and 9 lead to the preference for site of attack orderings for the chloroalkanes in Table 10. A number of trends can be noted:

(1) The metal ion (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 11). The $C\text{-}CH_2Cl$ 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 [91]. This bond is also approximately 4 kcal/mol stronger than the internal C-C bonds (Table 11).

(2) As the chain length of the alkyl chloride increases, metal ion insertion into internal C-C bonds becomes preferred over insertion into the

Table 11

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. 79-81.

[b] Calculated by using the group equivalence data in ref. 80.

C-Cl bond, which is the dominant site of insertion for the smaller chloroalkanes.

(3) There are a number of similarities between the preferred site of attack orderings for the chloroalkanes and their alkane analogs. For example, in both chlorohexane and hexane, Co^+ 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 chainlength 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_nH_{2n+1} bonds are formed. Note that $D(Co^+$-$C_nH_{2n+1})$ increases with increasing n [83].

(4) 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.

V. The 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 as ethanol. In the case of n-propanol (Table 8), Co^+ insertion into the C-OH bond accounts for only 70% of the products. Insertion into the C-C bonds leading to C_2H_4 and CH_4

elimination also occurs; these "alkane-like" reactions were not observed for either ethanol or 2-propanol. Ethylene elimination from n-propanol occurs through intermediate 24.

$$Co^+ + n\text{-}C_3H_7OH \longrightarrow \underset{24}{(C_2H_4)Co^+(CH_3OH)} \longrightarrow CoCH_3OH^+ + C_2H_4$$

This is consistent with the relative proton affinities ($PA(CH_3OH) > PA(C_2H_4)$) which would suggest that C_2H_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/mole stronger than the other skeletal bonds due to the presence of the OH group (Table 11). An exception is in the case of pentanol, where insertion into this C-C bond leads to the very stable $CoC_4H_6^+$.

For the larger alcohols, the $Co(H_2O)^+$ product was observed, but not the corresponding $Co(olefin)^+$ product. The larger olefins should have proton affinities greater than that of H_2O and thus, $Co(olefin)^+$ products should be observed. Since alcohols are hydrophilic, the presence of trace amounts of H_2O present cannot be ruled out, although it could not be detected. Thus, we cannot be certain that the small CoH_2O^+ 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_2O^+ ions are minor products.

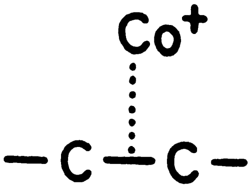
A number of observations concerning the ordering of preferred site of attack for the alcohols (Table 10) warrant discussion:

(1) As the alkyl chainlength increases, insertion into the C-OH bond

becomes a minor pathway and attack of C-C bonds dominates. In fact, if the CoH_2O^+ ions are due to trace amounts of water, then insertion into C-OH does not occur at all for the larger alcohols.

(2) 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.

(3) 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, 25, or by initial interaction of Co^+ with a C atom, 26,



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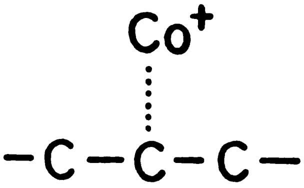

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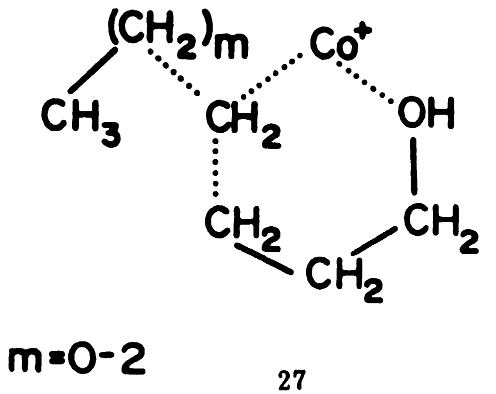
We assume the latter, 26. For small molecules such as ethanol, Co^+ initially complexes with a lone pair on the hydroxy group. This interaction weakens the C-OH bond making it susceptible for attack. If Co^+ interacts with a skeletal C atom, the bonds to that C atom become weakened and thus susceptible 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, due 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 (27,28) can be formed, 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.



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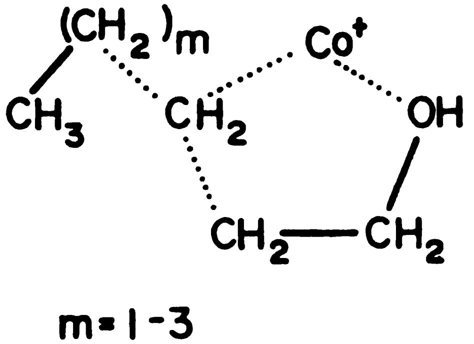

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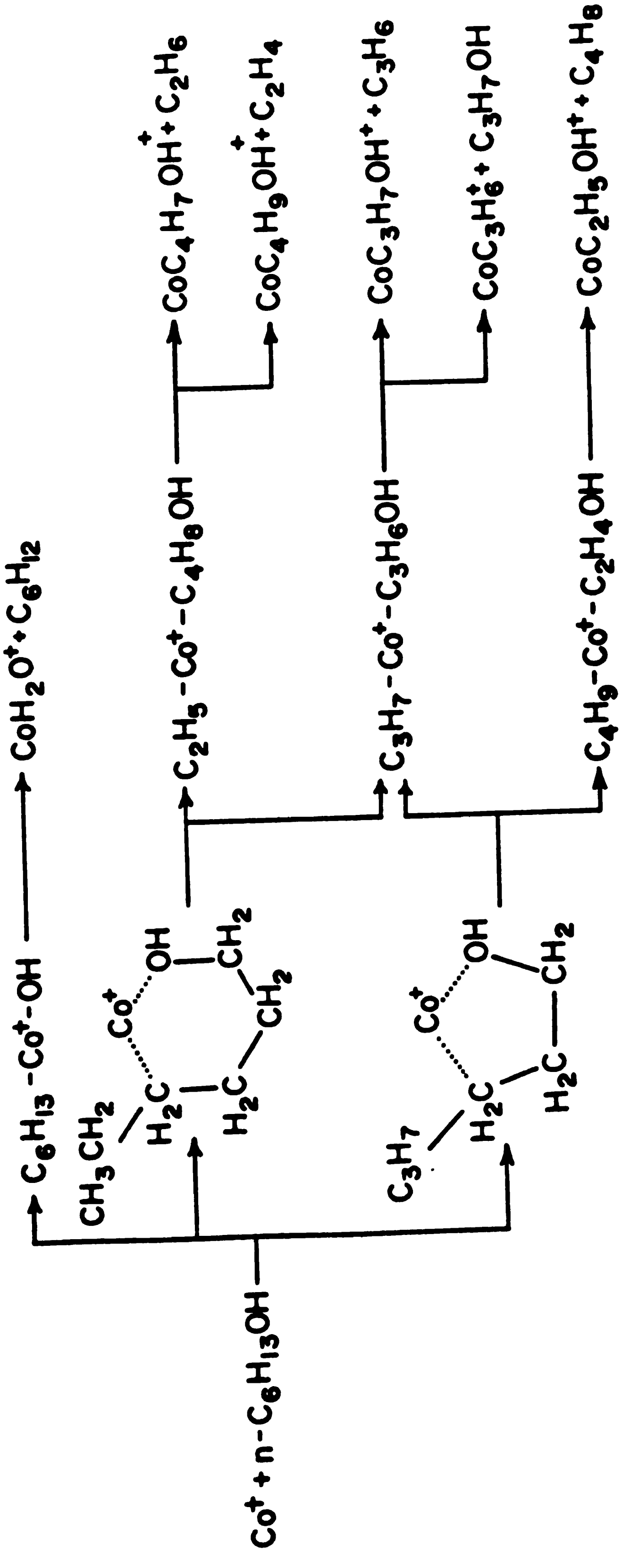
The formation of the five- and six-membered ring intermediates along with all of the possible insertion intermediates and the resulting products are shown in Scheme IX for 1-hexanol.

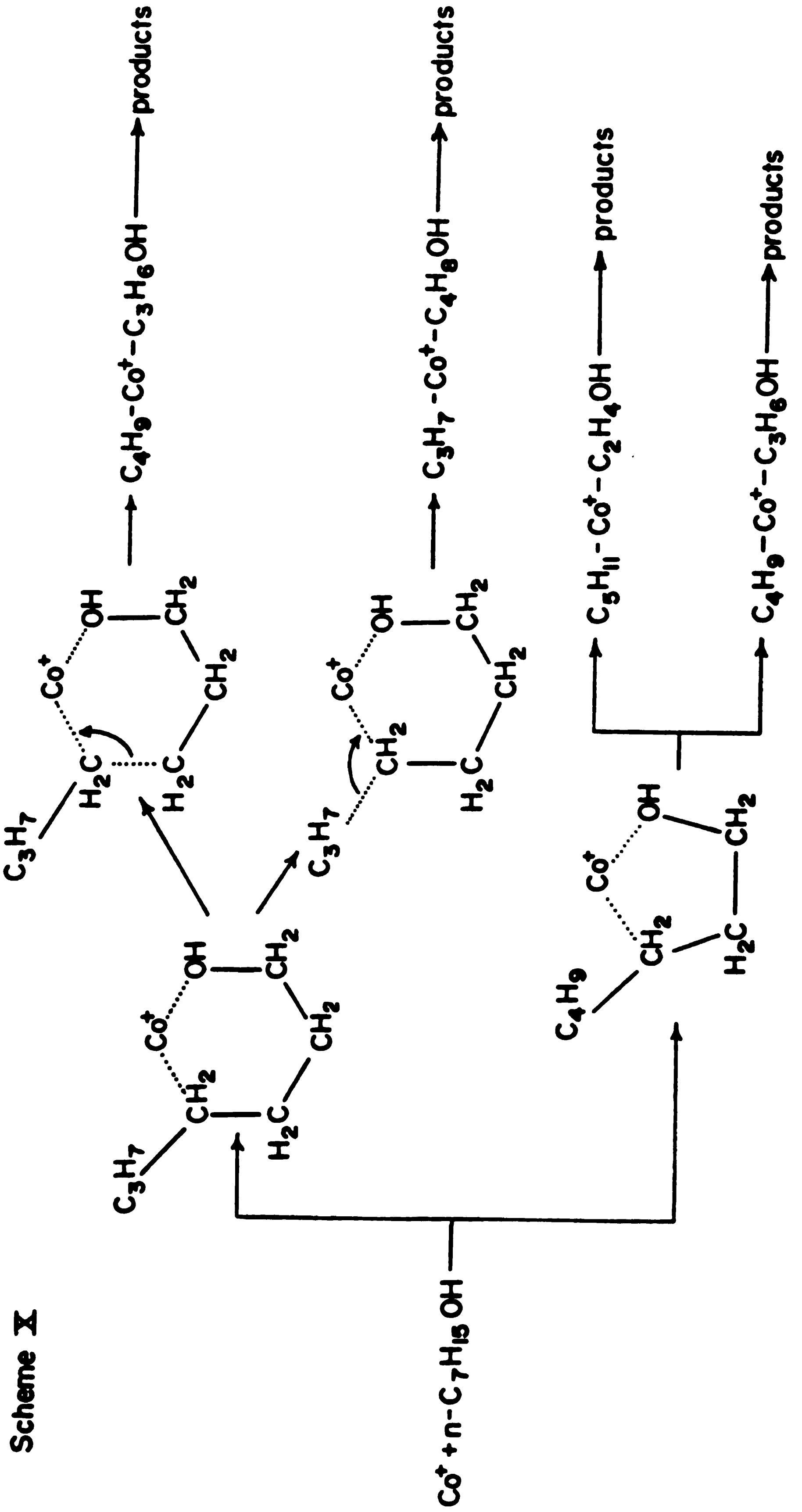
Using this model, which first become apparent in the case of 1-pentanol, all of the major products can be predicted for the longer chain ($n \geq 6$) alcohols. Scheme X uses the concept to show that it can be used to account for all of the major products of 1-heptanol. The reactions of octanol could also be explained in this way, allowing a 7-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

Scheme IX

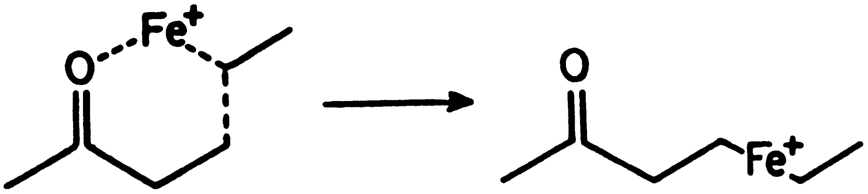

Co+ + n-C6H13OH
C6H13-Co+-OH
CoH2O+ + C6H12
CH3CH2
H2C
Co+
OH
CH2
CH2
CH2
H2C
C3H7
H2C
Co+
OH
CH2
H2C
C2H5-Co+-C4H8OH
C3H7-Co+-C3H6OH
C4H9-Co+-C2H4OH
CoC4H7OH+ + C2H6
CoC4H9OH+ + C2H4
CoC3H7OH+ + C3H6
CoC3H6+ + C3H7OH
CoC2H5OH+ + C4H8

Scheme X


Co⁺ + n-C₇H₁₅OH
C₃H₇
CH₂
Co⁺
OH
CH₂
CH₂
H₂C
C₃H₇
H₂C
Co⁺
OH
CH₂
CH₂
H₂C
C₃H₇
CH₂
Co⁺
OH
CH₂
CH₂
H₂C
C₄H₉-Co⁺-C₃H₆OH
products
C₃H₇-Co⁺-C₄H₈OH
products
C₄H₉
CH₂
Co⁺
OH
CH₂
H₂C
C₅H₁₁-Co⁺-C₂H₄OH
products
C₄H₉-Co⁺-C₃H₆OH
products

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 1-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 in 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 [3]. 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 [92].

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. [3] suggested such mechanisms to explain H_2 elimination reactions in the chemistry of Fe^+ with labelled ketones, in which Fe^+ complexes with the carbonyl oxygen and inserts into C-H bonds via 5- and 6-membered ring intermediates.

VI. The Chemistry of CoL_x^+ with 1-Chloro- and 1-Hydroxy-n-Alkanes

We have mentioned earlier that whenever metal ions M^+ are generated by electron impact on volatile metal carbonyls, $M(CO)_x^+$ ions are formed as well. In the case of $Co(CO)_3NO$, the low pressure 70 eV EI mass spectrum contains $Co(CO)_x^+$ (x = 0-2) and $Co(CO)_xNO^+$ (x = 0-3) ions. Some of these ions also react with neutral organic molecules in a way similar to Co^+. Consider the chemistry of $CoCO^+$, $Co(CO)_2^+$ and $CoCONO^+$ with 2-chloropropane [19]:

$$\begin{array}{lll} CoCO^+ + i\text{-}C_3H_7Cl & \longrightarrow CoCOC_3H_6^+ + HCl & (16\%) \\ & \longrightarrow CoC_3H_6^+ + HCl + CO & (67\%) \\ & \longrightarrow CoCOHCl^+ + C_3H_6 & (17\%) \end{array}$$

$$Co(CO)_2^+ + i\text{-}C_3H_7Cl \longrightarrow CoCOC_3H_6^+ + HCl + CO \qquad (100\%)$$

$$\begin{array}{lll} CoCONO^+ + i\text{-}C_3H_7Cl & \longrightarrow CoNOC_3H_6^+ + HCl + CO & (53\%) \\ & \longrightarrow CoNOC_3H_7Cl^+ + CO & (47\%) \end{array}$$

We can see that all three metal-containing ions ($CoCO^+$, $Co(CO)_2^+$ and $CoCONO^+$) induce the dehydrohalogenation reaction, a process also observed for the bare metal ion, Co^+. The last reaction of $CoCONO^+$ with

2-chloropropane is a ligand displacement reaction.

Tables 12 and 13 list the products observed for the reactions of the electron impact fragments of $Co(CO)_3NO$ with the series of 1-chloro- and 1-hydroxy-n-alkanes respectively. The results in these tables can supply valuable information on "ligand effects", i.e., how and why the CO and NO ligands bound to the metal center affect its chemistry with monofunctional organic molecules. This information can be supplied by evaluating the results in Tables 12 and 13 and identifying: (1) The changes in the chemistry exhibited by the metal center when one or more ligands are added sequentially. (2) The changes in the chemistry of the metal center due to an increase in the alkyl chain length of the organic molecule.

1-Chloro-n-Alkanes. The reaction pathways observed for the CoL_x^+ ions with the C_3-C_8 chloroalkanes are typical for metal-containing ions in their chemistry with monofunctional organic molecules, in the following ways: (1) The bare metal ion reacts to form the largest variety of products [19,20]. (2) The organic rearrangement processes observed for $CoCO^+$ are similar to those observed for Co^+ [20,26,34,35]. For example, in the case of Co^+ and $CoCO^+$ reacting with 1-chloropropane, products coming from similar mechanistic processes are observed (Tables 8 and 12):

$$\begin{array}{llll}
\mathrm{Co^+ + C_3H_7Cl} & \longrightarrow & \mathrm{C_3H_7^+ + CoCl} & (72\%) \\
 & \longrightarrow & \mathrm{CoC_3H_6^+ + HCl} & (23\%) \\
 & \longrightarrow & \mathrm{CoHCl^+ + C_3H_6} & (5\%)
\end{array}$$

$$\begin{array}{llll}
\mathrm{CoCO^+ + C_3H_7Cl} & \longrightarrow & \mathrm{CoC_3H_6^+ + HCl + CO} & (54\%) \\
 & \longrightarrow & \mathrm{CoCOHCl^+ + C_3H_6} & (13\%) \\
 & \longrightarrow & \mathrm{CoCOC_3H_6^+ + HCl} & (16\%) \\
 & \longrightarrow & \mathrm{CoCOC_3H_7Cl^+} & (17\%)
\end{array}$$

Table 12

Reaction Products of CoL_x^+ with 1-Chloro-n-Alkanes

	P (parent)					
Reactant						
$CoCO^+$	$CoC_3H_6^+ + HCl + CO$	(0.54)	$CoCOC_4H_8^+ + HCl$	(0.60)	$CoC_3H_6^+ + C_2H_5Cl + CO$	(0.07)
	$CoCOHCl^+ + C_3H_6$	(0.13)	$CoCOHCl^+ + C_4H_8$	(0.40)	$CoC_5H_{10}^+ + HCl + CO$	(0.60)
	$CoCOC_3H_6^+ + HCl$	(0.16)			$CoCOC_5H_{10}^+ + HCl$	(0.33)
	$CoCOP^+$	(0.17)				
$Co(CO)_2^+$	$CoCOC_3H_6^+ + HCl + CO$	(0.41)	$CoCOC_4H_8^+ + HCl + CO$	(1.00)	$CoCOC_5H_{10}^+ + HCl + CO$	(0.45)
	$CoCOP^+ + CO$	(0.59)			$CoCOP^+ + CO$	(0.55)
$CoNO^+$	NR		NR		NR	
$CoCONO^+$	$CoNOC_3H_6^+ + HCl + CO$	(0.55)	NR		NR	
	$CoNOP^+ + CO$	(0.45)				
$Co(CO)_2NO^+$	$CoNOP^+ + 2CO$	(0.47)	$CoNOP^+ + 2CO$	(0.69)	$CoNOP^+ + 2CO$	(0.83)
	$CoCONOP^+ + CO$	(0.53)	$CoCONOP^+ + CO$	(0.31)	$CoCONOP^+ + CO$	(0.17)
$Co(CO)_3NO^+$	$CoCONOP^+ + 2CO$	(0.28)	$CoCONOP^+ + 2CO$	(1.00)	$CoCONOP^+ + 2CO$	(0.51)
	$Co(CO)_2NOP^+ + CO$	(0.72)			$Co(CO)_2NOP^+ + CO$	(0.49)

Table 12 continues

Table 12 continued

	P (parent)					
Reactant						
CoCO$^+$	$CoC_6H_{12}^+$ + HCl + CO	(1.00)	$CoC_5H_{10}^+$ + C_2H_5Cl + CO	(0.17)	$CoC_5H_{10}^+$ + C_3H_7Cl + CO	(0.07)
			$CoC_7H_{14}^+$ + HCl + CO	(0.73)	$CoC_6H_{12}^+$ + C_2H_5Cl + CO	(0.17)
			$CoCOC_7H_{14}^+$ + HCl	(0.10)	$CoC_8H_{16}^+$ + HCl + CO	(0.53)
					$CoCOC_8H_{16}^+$ + HCl	(0.03)
					CoP$^+$ + CO	(0.07)
					CoCOP$^+$	(0.13)
$Co(CO)_2^+$	$CoC_6H_{12}^+$ + HCl + 2CO	(0.18)	$CoC_7H_{14}^+$ + HCl + 2CO	(0.27)	$CoC_8H_{16}^+$ + HCl + 2CO	(0.35)
	$CoCOC_6H_{12}^+$ + HCl + CO	(0.42)	$CoCOC_7H_{14}^+$ + HCl + CO	(0.27)	$CoCOC_8H_{16}^+$ + HCl + CO	(0.08)
	CoCOP$^+$ + CO	(0.40)	CoCOP$^+$ + CO	(0.46)	CoP$^+$ + 2CO	(0.24)
					CoCOP$^+$ + CO	(0.33)
CoNO$^+$	NR		NR		NR	
CoCONO$^+$	NR		NR		CoNOP$^+$ + CO	(1.00)
$Co(CO)_2NO^+$	CoNOP$^+$ + 2CO	(0.89)	CoNOP$^+$ + 2CO	(0.91)	CoNOP$^+$ + 2CO	(1.00)
	CoCONOP$^+$ + CO	(0.11)	CoCONOP$^+$ + CO	(0.09)		
$Co(CO)_3NO^+$	CoNOP$^+$ + 3CO	(0.09)	CoCONOP$^+$ + 2CO	(1.00)	CoCONOP$^+$ + 2CO	(1.00)
	CoCONOP$^+$ + 2CO	(0.64)				
	$Co(CO)_2NOP^+$ + CO	(0.27)				

Table 13

Reaction Products of CoL_x^+ with 1-Hydroxy-n-Alkanes

	P (parent)					
Reactant						
$CoCO^+$	$CoC_3H_6O^+ + H_2 + CO$	(0.06)	$CoCOC_4H_8O^+ + H_2$	(0.06)	$CoC_3H_7OH^+ + C_2H_4 + CO$	(0.26)
	$CoP^+ + CO$	(0.65)	$CoC_4H_8O^+ + H_2 + CO$	(0.34)	$CoC_5H_{10}O^+ + H_2 + CO$	(0.24)
	$CoCOP^+$	(0.29)	$CoC_4H_8^+ + H_2O + CO$	(0.10)	$CoP^+ + CO$	(0.24)
			$CoH_2O^+ + C_4H_8 + CO$	(0.07)	$CoCOP^+$	(0.26)
			$CoCOH_2O^+ + C_4H_8$	(0.08)		
			$CoC_2H_3OH^+ + C_2H_6 + CO$	(0.04)		
			$CoP^+ + CO$	(0.31)		
$Co(CO)_2^+$	$CoCOP^+ + CO$	(1.00)	$CoCOC_4H_8O^+ + H_2 + CO$	(0.10)	$CoP^+ + 2CO$	(0.28)
			$CoCOH_2O^+ + C_4H_8 + CO$	(0.09)	$CoCOP^+ + CO$	(0.72)
			$CoCOP^+ + CO$	(0.53)		
			$CoP^+ + 2CO$	(0.28)		
$CoNO^+$	$CoNOH_2O^+ + C_3H_6$	(0.37)	$CoNOH_2O^+ + C_4H_8$	(1.00)	$CoNOC_3H_6^+ + C_2H_5OH$	(0.26)
	$CoNOP^+$	(0.63)			$CoNOP^+$	(0.74)
$CoCONO^+$	$CoNOP^+ + CO$	(1.00)	$CoNOH_2O^+ + C_4H_8 + CO$	(0.20)	$CoNOP^+ + CO$	(1.00)
			$CoNOP^+ + CO$	(0.80)		
$Co(CO)_2NO^+$	$CoNOP^+ + 2CO$	(1.00)	$CoNOH_2O^+ + C_4H_8 + 2CO$	(0.04)	$CoNOP^+ + 2CO$	(1.00)
			$CoNOC_4H_8O^+ + H_2 + 2CO$	(0.12)		
			$CoNOP^+ + 2CO$	(0.84)		
$Co(CO)_3NO^+$	$CoCONOP^+ + 2CO$	(1.00)	$CoCONOC_4H_8O^+ + H_2 + 2CO$	(0.14)	$CoNOP^+ + 3CO$	(0.25)
			$CoCONOP^+ + 2CO$	(0.86)	$CoCONOP^+ + 2CO$	(0.75)

Table 13 continues

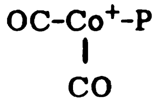
Table 13 continued

Reactant	P (parent)					
						
$CoCO^+$	$CoC_3H_6^+ + C_3H_7OH + CO$	(0.09)	$CoC_2H_5OH^+ + C_5H_{10} + CO$	(0.02)	$CoC_5H_{10}^+ + C_3H_7OH + CO$	(0.14)
	$CoC_2H_5OH^+ + C_4H_8 + CO$	(0.07)	$CoC_4H_8^+ + C_3H_7OH + CO$	(0.19)	$CoC_4H_7OH^+ + C_4H_{10} + CO$	(0.21)
	$CoC_3H_7OH^+ + C_3H_6 + CO$	(0.21)	$CoC_3H_7OH^+ + C_4H_8 + CO$	(0.09)	$CoC_4H_9OH^+ + C_4H_8 + CO$	(0.16)
	$CoC_4H_7OH^+ + C_2H_6 + CO$	(0.18)	$CoC_4H_7OH^+ + C_3H_8 + CO$	(0.23)	$CoC_5H_{11}OH^+ + C_3H_6 + CO$	(0.02)
	$CoC_4H_9OH^+ + C_2H_4 + CO$	(0.06)	$CoC_4H_9OH^+ + C_3H_6 + CO$	(0.11)	$CoC_8H_{16}O^+ + H_2 + CO$	(0.13)
	$CoCOC_6H_{12}O^+ + H_2$	(0.06)	$CoP^+ + CO$	(0.31)	$CoP^+ + CO$	(0.26)
	$CoC_6H_{12}O^+ + H_2 + CO$	(0.08)	$CoCOP^+$	(0.05)	CoP^+	(0.08)
	$CoP^+ + CO$	(0.25)				
$Co(CO)_2^+$	$CoC_6H_{12}O^+ + H_2 + 2CO$	(0.11)	$CoP^+ + 2CO$	(0.85)	$CoC_8H_{16}O^+ + H_2 + 2CO$	(0.11)
	$CoCOC_6H_{12}O^+ + H_2 + CO$	(0.24)	$CoCOP^+ + CO$	(0.15)	$CoP^+ + 2CO$	(0.63)
	$CoP^+ + 2CO$	(0.45)			$CoCOP^+ + CO$	(0.26)
	$CoCOP^+ + CO$	(0.20)				
$CoNO^+$	$CoNOH_2O^+ + C_6H_{12}$	(1.00)	NR		NR	
$CoCONO^+$	$CoNOC_6H_{12}O^+ + H_2 + CO$	(0.30)	$CoNOP^+ + CO$	(1.00)	$CoNOC_8H_{16}O^+ + H_2 + CO$	(0.06)
	$CoNOP^+ + CO$	(0.70)			$CoNOP^+ + CO$	(0.94)
$Co(CO)_2NO^+$	$CoNOC_6H_{12}O^+ + H_2 + 2CO$	(0.20)	$CoNOP^+ + 2CO$	(1.00)	$CoNOC_8H_{16}O^+ + H_2 + 2CO$	(0.04)
	$CoNOP^+ + 2CO$	(0.80)			$CoNOP^+ + 2CO$	(0.96)
$Co(CO)_3NO^+$	$CoCONOC_6H_{12}O^+ + H_2 + 2CO$	(0.44)	$CoNOP^+ + 3CO$	(0.56)	$CoCONOC_8H_{16}O^+ + H_2 + 2CO$	(0.31)
	$CoNOP^+ + 3CO$	(0.23)	$CoCONOP^+ + 2CO$	(0.44)	$CoCONOP^+ + 2CO$	(0.69)
	$CoCONOP^+ + 2CO$	(0.33)				

For the $CoCO^+$ ion, it can be seen that metal insertion into the C-Cl bond leads to the majority of the products observed. The only difference is the formation of the alkyl cation $C_3H_7^+$ via chloride abstraction, which is *not* observed for the $CoCO^+$ ion; this lack of formation of the corresponding alkyl cation is observed throughout the series of chloroalkanes studied. The implication is that IP(CoCOCl) < IP(CoCl).

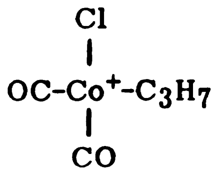
As the alkyl chain length of the chloroalkanes increases (n > 4), metal ion insertion into internal C-C bonds starts to occur, followed by a β-H shift leading to the intermediate (alkene)Co^+(CO)(chloroalkane). Since CO and chloroalkanes have lower proton affinities than alkenes, they are both preferentially lost in every case (Table 12). Note that in the case of the $CoCO^+$ ion, the C-C bonds which the metal ion inserts are the most preferred site(s) of attack for the bare metal ion Co^+ (Table 10). **(3)** In contrast with the $CoCO^+$ ion, no products are observed for the $CoNO^+$ ion with the series of chloroalkanes studied. This deactivation of the metal center by an NO ligand have been previously reported [14,20,34,35]. **(4)** As the number of ligands present on the metal ion increases, ligand substitution reactions in which one or more CO's are displaced by an organic molecule become the predominant process [19,20]. Whenever a reaction occurs where a carbonyl group is the only elimination product, the product ion structure has to be determined. For example, does the $CoCOP^+$ product ion contains P as an intact molecule or in the form of A-B, where A and B are fragments or rearrangement products of the organic molecule P?

In the case of $Co(CO)_2^+$ reacting with 1-chloropropane to form the $CoCOP^+$ product ion, possible structures for the intermediate are:



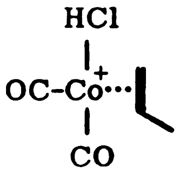
$$\mathrm{OC{-}\underset{\displaystyle CO}{\underset{|}{Co^{+}}}{-}P}$$

29



$$\mathrm{OC{-}\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CO}{\underset{|}{Co^{+}}}}}{-}C_3H_7}$$

30



31

In structure 29, loss of a CO group leads to the formation of the $CoCOP^+$ product ion (a ligand displacement reaction). In structure 30, both C_3H_7 and Cl groups are strongly bound to the metal center [36]. Therefore CO should be lost, which gives us no evidence for any possible structural rearrangement. Structure 31 would not be expected, since in that case loss of the weakly bound ligands CO and HCl would occur, leading to the formation of $CoCOC_3H_6^+$ product ion instead of the $CoCOP^+$ ion.

Throughout this dissertation, it is assumed that loss of 28 u corresponds to loss of a CO molecule and that the organic molecule is intact on the product ion (of the type $Co(CO)_x(NO)_yP^+$, $x = 1,2$ and $y = 0,1$) unless otherwise mentioned. However, one should realize, that for ions such as $CoCO^+$, $Co(CO)_2^+$ and $CoCONO^+$ whenever a CO is lost in a ligand displacement reaction, there is a high probability for the product ion to be a mixture of CoP^+ and $Co(A)(B)^+$, while for the $Co(CO)_2NO^+$ and $Co(CO)_3NO^+$ ions the parent molecule is most likely intact because no empty orbitals are available on the metal, which can be used to rearrange the parent molecule.

1-Hydroxy-n-Alkanes

The chemistry exhibited by CoL_x^+ with the C_3-C_8 1-alcohols is much richer compared to that of the chloroalkanes (Tables 12,13): **(1)** The bare metal ion is not the only ionic species that forms the largest variety of products, since the $CoCO^+$ ion also reacts to form the same products through identical rearrangement processes. For example in the case of $CoCO^+$ reacting with 1-butanol, metal insertion into the C-OH and C-C bonds occurs to lead to the formation of products similar to those observed for the bare metal ion Co^+ (Tables 8,13).

A unique reaction occurs for 1-propanol. The mixture of $Co(CO)_3NO$ and 1-propanol, when subject to electron impact, produces $Co(C_3H_6O)^+$. Ion cyclotron double resonance indicates that $CoCO^+$ is the precursor of this dehydrogenation product, and not Co^+. We believe this is an example of active participation of the CO ligand in the reaction and $CoCO^+$ insertion occurs instead of that of Co^+ [20,34,35]. Since the elimination of both H_2 and CO is observed in the above mentioned reaction, this may indicate that H_2CO is lost from the reaction's intermediate. An additional indication for the "formation" of H_2CO is provided by a subsequent reaction of $CoCONO(C_3H_7OH)^+$ with the parent molecule of C_3H_7OH:

$$CoCONO(C_3H_7OH)^+ + C_3H_7OH \longrightarrow CoNO(C_3H_6O)(C_3H_7OH)^+ + H_2CO$$

Similar "storage" of an H_2 molecule on a CO ligand (forming H_2CO) may occur for all the alcohols studied, whenever loss of both H_2 and CO is observed [93]. **(2)** An increase in the alkyl chain length in the case of alcohols, has a more "dramatic" effect on the reaction products. This might be due to a relatively strong initial cobalt ion-alcohol interaction on complexation, since

PA(alcohols) > PA(chloroalkanes). In the case of the $CoCO^+$ ion reacting with 1-alcohols, as the alkyl chain length increases, insertion into the C-OH bond becomes less dominant; a behavior, identical to that observed for the bare metal ion. **(3)** The $CoNO^+$ ion is reactive in the case of small alcohols ($n \leq 6$), giving rise to either direct attachment products ($CoNOP^+$) or products coming through metal insertion into the polar C-OH bond. In the case of 1-propanol, metal insertion into the C-OH bond leads to the formation of the $CoNOH_2O^+$ product ion by eliminating the corresponding olefin, C_3H_6. From the proton affinities/metal-ion affinities trends, one would expect the olefin to be retained more by the metal but it is the H_2O which is retained more. One possible explanation is that $CoNO^+$ insertion into the C-OH bond occurs instead of Co^+ insertion, in analogy to the $CoCO^+$ insertion process mentioned above. Metal-NO insertions occurring in condensed phases have been previously discussed in a review by McCleverty [94]. **(4)** As in the case of chloroalkanes, "ligand substitution" reactions are dominant as the number of ligands on the metal ion increases. Insights into the product ion structure can be provided by subsequent reactions of the ion of interest [19,20]. For example in the case of 1-propanol, the following series of reactions is observed:

$$CoCO^+ + C_3H_7OH \longrightarrow Co(C_3H_7OH)^+ + CO \qquad (23)$$

$$Co(C_3H_7OH)^+ + C_3H_7OH \longrightarrow Co(C_3H_6)(C_3H_7OH)^+ + H_2O \qquad (24)$$

In reaction (23), a ligand substitution process, a complex between Co^+ and propanol is formed. The further reaction of the product in (23), reaction (24), implies that the product of (23) exist as:

$(H_2O)Co^+(C_3H_6)$

Thus $CoCO^+$ reacts with C_3H_7OH to form $Co(C_3H_6)(H_2O)^+$ which reacts further in (24) by a simple ligand substitution in which a second molecule of C_3H_7OH displaces the more weakly bound H_2O from the metal center. **(5)** An interesting reaction observed for the $Co(CO)_xNO^+$ ions (x = 1-3) is the elimination of H_2 along with a number of CO ligands. This reaction observed for $Co(CO)_{2,3}NO^+$ cannot go through intermediates with all ligands bound on the metal; i.e., reactions must proceed through a series of ligand losses and metal-induced reactions. That is, intermediates such as $Co(CO)_3NO(C_4H_8O)(H_2)^+$ - in the case of $Co(CO)_3NO^+$ reacting with 1-butanol - would not be expected, since that violates the 18-electron rule. This dehydrogenation process is observed only for n-alcohols with a four, six and eight carbon chain length (Table 13), for reason(s) that we cannot explain at the present time.

One should realize that, "ligand effects" is only a partially studied area of gas phase organometallic chemistry; however it is a new active area of research in our laboratory. We are currently attempting to formulate some rules such that the observed differences in the chemistry of M^+ and ML_x^+ with various organic compounds could be explained and the products formed in each case could be predicted as well.

Our current level of understanding will be best presented by discussing the "ligand effects" in the case of CoL_x^+ with alkanes [77]. Consider the chemistry of Co^+ and $CoCO^+$ with alkanes larger than ethane. For Co^+ metal insertion into C-C bonds is a dominant process while for $CoCO^+$ along with "ligand substitution" reactions, a preferred metal insertion into C-H bonds is also observed. That preference for C-H insertion over C-C insertion may be a steric effect.

Consider the intermediates of the Co^+ insertion into a C-C or a C-H bond of an alkane:

$R\text{-}CO^{+}\text{-}R'$

32

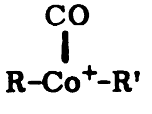
$R''\text{-}Co^{+}\text{-}H$

33

The energy required for insertion into the C-C bond, i.e., formation of the intermediate 32 is:

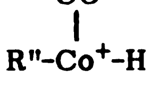
$$\Delta H_{\text{insertion}} = D(R\text{-}R') - \underbrace{[D(Co^{+}\text{-}R) + D(RCo^{+}\text{-}R')]}_{A} + E_s \qquad (16)$$

where E_s is the energy released due to steric effects. For the intermediate 33, the term A containing the bond strengths of the new formed bonds becomes smaller than the one in equation (16) but at the same time E_s is smaller too. Therefore, there is a competition between the two terms A and E_s, and depending on the net effect a preferred metal insertion into a C-C or a C-H bond occurs. For the Co^+ ion, insertion into the C-C bonds is dominant (E_s is small). In the case of the $CoCO^+$ ion, there is a number of possibilities for the insertion intermediate:



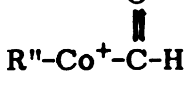
$R\text{-}\overset{CO}{\overset{|}{Co}}{}^{+}\text{-}R'$

34



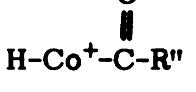
$R''\text{-}\overset{CO}{\overset{|}{Co}}{}^{+}\text{-}H$

35



$R''\text{-}Co^{+}\text{-}\overset{O}{\overset{\|}{C}}\text{-}H$

36

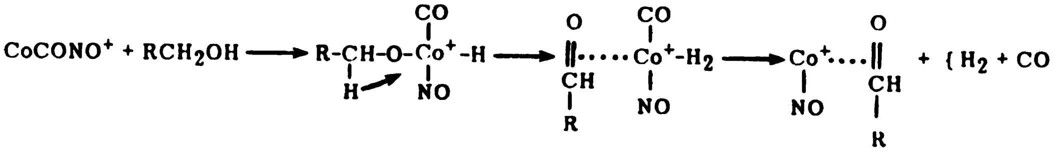


$H\text{-}Co^{+}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R''$

37

Since the most preferred insertion intermediate is that which is the more stable thermodynamically, M^+-C and M^+-H bond strengths would suggest that insertion into C-C bonds is preferred. However, steric effects (E_s) associated with the C-C insertion intermediate, 34, may be more significant than E_s associated with the C-H insertion intermediate, 35, leading to a preference by $CoCO^+$ for insertion into a terminal C-H bond. Intermediates 36 and 37 involve an active participation of the CO ligand in the reaction. Thermochemical estimates suggest that $CoCO^+$ insertion into C-H bonds is favored, due to the energy released upon formation of the HCO ligand (intermediate 36). However, results of $NiCO^+$ and $NiPF_3^+$ with nonane [77] indicate that insertion of MCO^+ into C-H bonds is not a requirement for H_2 elimination. Therefore in the case of alkanes, metal insertion into the terminal C-H bond would be favored, intermediate 35 (low E_s), leading to H_2 elimination.

In the case of alcohols (present work), H_2 elimination occurs along with loss of one CO in the case of the $CoCONO^+$ reactant ion and two CO's in the case of $Co(CO)_{2,3}NO^+$ ions. This may be an implication of a mechanism involving insertion of the $CoCO^+$ ion into a terminal C-H bond (through an intermediate similar to 36). However, the possibility of metal insertion into the O-H bond leading to intermediate 38, followed by a β-H shift leading to elimination of H_2 and CO (probably in the form of H_2CO [93]) has to be considered as well (reaction 25).



$$CoCONO^+ + RCH_2OH \longrightarrow R\text{-}\underset{H}{CH}\text{-}O\text{-}\overset{CO}{\underset{NO}{Co^+}}\text{-}H \longrightarrow \underset{\underset{R}{CH}}{\overset{O}{\|}}\cdots\overset{CO}{\underset{NO}{Co^+}}\text{-}H_2 \longrightarrow \underset{NO}{Co^+}\cdots\underset{\underset{R}{CH}}{\overset{O}{\|}} + \{H_2 + CO\} \qquad (25)$$

38

Since H_2 elimination is observed *only* for alcohols and not for chloroalkanes (Tables 12,13), metal insertion into the O-H bond is most likely the major mechanistic pathway leading to H_2 elimination.

CHAPTER 5

THE CHEMISTRY OF COBALT-CONTAINING IONS WITH A SERIES OF n-CHLORO-1-ALCOHOLS AND 1-BROMO-n-CHLORO-ALKANES

I. The Chemistry of Co^+ with n-Chloro-1-Alcohols and 1-Bromo-n-Chloro-Alkanes

In this work, the gas phase chemistry of Co^+ with a series of bifunctional organic molecules, haloalcohols and dihaloalkanes, containing two to six carbon atoms is presented. The results of these experiments are listed in Tables 14 and 15. These studies can provide insights into the combined effect of the chain length and the functional group on the chemistry exhibited by the metal ion, Co^+.

Unfortunately, insights into the ordering for preferred site of attack of skeletal bonds are difficult to obtain. That is because little information is known about the mechanism by which some of the major products are formed, i.e., where the metal ion inserts. This makes it difficult to derive a suggested order of preference for site of attack of skeletal C-C bonds by Co^+. Take as an example the case of 5-chloro-1-pentanol reacting with Co^+. There are four C-C bonds, one C-OH bond and one C-Cl bond into which Co^+ may insert:

Table 14

Reaction Products Observed for ω-Chloro-1-Alcohols with Co^+-Containing Ions

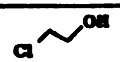
Reactant	P (parent)					
						
Co^+	$C_2H_4OH^+ + CoCl$	(0.27)	$CoC_3H_4^+ + HCl + H_2O$	(0.32)	$CoC_4H_6^+ + HCl + H_2O$	(0.59)
	$CoH_2O^+ + C_2H_3Cl$	(0.02)	$CoC_2H_2O^+ + H_2 + CH_3Cl$	(0.06)	$CoC_2H_2O^+ + H_2 + C_2H_5Cl$	(0.35)
	$CoC_2H_2^+ + HCl + H_2O$	(0.08)	$CoC_3H_5OH^+ + HCl$	(0.35)	$CoC_4H_8O^+ + HCl$	(0.06)
	$CoC_2H_3OH^+ + HCl$	(0.22)	$CoC_3H_5Cl^+ + H_2O$	(0.09)		
	$CoClOH^+ + C_2H_4$	(0.41)	$CoC_3H_5OCl^+ + H_2$	(0.04)		
			CoP^+	(0.14)		
$CoCO^+$	$C_2H_4OH^+ + CoCl + CO$	(0.08)	$CoC_3H_5OH^+ + HCl + CO$	(0.66)	$CoCOC_4H_8O^+ + HCl$	(0.19)
	$CoC_2H_3OH^+ + HCl + CO$	(0.64)	$CoC_3H_5OCl^+ + H_2 + CO$	(0.04)	$CoC_4H_8O^+ + HCl + CO$	(0.53)
	$CoC_2H_4OH^+ + Cl + CO$	(0.04)	$CoP^+ + CO$	(0.16)	$CoC_4H_6^+ + HCl + H_2O + CO$	(0.13)
	$CoCOH_2O^+ + C_2H_3Cl$	(0.02)	$CoCOP^+$	(0.14)	$CoCH_3OH^+ + C_3H_5Cl + CO$	(0.15)
	$CoCOC_2H_3OH^+ + HCl$	(0.04)				
	$CoP^+ + CO$	(0.09)				
	$CoCOP^+$	(0.05)				
	m/z 133	(0.04)				
$Co(CO)_2^+$	$CoP^+ + 2CO$	(0.40)	$CoP^+ + 2CO$	(0.76)	$CoCOC_4H_8O^+ + HCl + CO$	(0.77)
	$CoCOP^+ + CO$	(0.60)	$CoCOP^+ + CO$	(0.24)	$CoCOCH_3OH^+ + C_3H_5Cl + CO$	(0.23)
$CoNO^+$	$CoNOP^+$	(1.00)	N.R.		N.R.	
$CoCONO^+$	$CoNOC_2H_3OH^+ + HCl + CO$	(0.36)	$CoNOC_3H_5OH^+ + HCl + CO$	(0.19)	N.R.	
	$CoNOP^+ + CO$	(0.64)	$CoNOC_2H_3Cl^+ + CH_3OH + CO$	(0.12)		
			$CoNOP^+ + CO$	(0.48)		
			$CoCONOP^+$	(0.21)		
$Co(CO)_2NO^+$	$CoNOP^+ + 2CO$	(1.00)	$CoCONOC_2H_3Cl^+ + CH_3OH + CO$	(0.04)	$CoNOC_4H_8O^+ + HCl + 2CO$	(0.82)
			$CoNOC_3H_5OCl^+ + H_2 + 2CO$	(0.04)	$CoNOP^+ + 2CO$	(0.07)
			$CoNOP^+ + 2CO$	(0.89)	$CoCONOCH_3OH^+ + C_3H_5Cl + CO$	(0.04)
			$CoCONOP^+ + CO$	(0.03)	$CoNOCH_3OH^+ + C_3H_5Cl + 2CO$	(0.07)
$Co(CO)_3NO^+$	$CoCONOP^+ + 2CO$	(1.00)	$CoCONOC_2H_3Cl^+ + CH_3OH + 2CO$	(0.04)	$CoCONOC_4H_8O^+ + HCl + 2CO$	(0.45)
			$CoNOP^+ + 3CO$	(0.81)	$CoNOP^+ + 3CO$	(0.29)
			$CoCONOP^+ + 2CO$	(0.15)	$CoCONOCH_3OH^+ + C_3H_5Cl + 2CO$	(0.26)

Table 14 continues

Table 14 continued

Reactant	P (parent)			
				
Co^+	$CoC_3H_4^+ + (C_2H_5Cl + H_2O$ or $C_2H_5OH + HCl)$	(0.06)	$CoC_3H_4^+ + (C_3H_7Cl + H_2O$ or $C_3H_7OH + HCl)$	(0.04)
	$CoC_2H_2O^+ + H_2 + C_3H_7Cl$	(0.08)	$CoC_2H_2O^+ + H_2 + C_4H_9Cl$	(0.03)
	$CoC_4H_6^+ + (CH_3Cl + H_2O$ or $CH_3OH + HCl)$	(0.23)	$CoC_4H_6^+ + (C_2H_5Cl + H_2O$ or $C_2H_5OH + HCl)$	(0.13)
	$CoC_3H_5OH^+ + C_2H_5Cl$	(0.12)	$CoC_3H_5OH^+ + C_3H_7Cl$	(0.39)
	$CoC_5H_8^+ + HCl + H_2O$	(0.09)	$CoC_4H_7OH^+ + C_2H_5Cl$	(0.12)
	$CoC_3H_5Cl^+ + C_2H_5OH$	(0.42)	$CoC_3H_7Cl^+ + C_3H_5OH$	(0.15)
			$CoC_6H_{10}^+ + HCl + H_2O$	(0.05)
			$CoC_6H_{12}O^+ + HCl$	(0.09)
$CoCO^+$	$CoC_5H_{10}O^+ + HCl + CO$	(1.00)	$CoC_3H_5OH^+ + C_3H_7Cl + CO$	(0.28)
			$CoC_4H_7OH^+ + C_2H_5Cl + CO$	(0.20)
			$CoC_6H_{10}^+ + HCl + H_2O + CO$	(0.20)
			$CoC_6H_{12}O^+ + HCl + CO$	(0.18)
			$CoP^+ + CO$	(0.09)
			$CoCOP^+$	(0.05)
$Co(CO)_2^+$	$CoCOC_5H_{10}O^+ + HCl + CO$	(1.00)	$CoP^+ + 2CO$	(0.40)
			$CoCOP^+ + CO$	(0.12)
			$CoCOC_4H_7OH^+ + C_2H_5Cl + CO$	(0.48)
$CoNO^+$	N.R.		N.R.	
$CoCONO^+$	$CoNOC_5H_{10}O^+ + HCl + CO$	(1.00)	$CoNOC_6H_{12}O^+ + HCl + CO$	(1.00)
$Co(CO)_2NO^+$	$CoNOC_5H_{10}O^+ + HCl + 2CO$	(0.61)	$CoNOC_6H_{11}OCl^+ + H_2 + 2CO$	(0.05)
	$CoCONOC_5H_{10}O^+ + HCl + CO$	(0.09)	$CoNOP^+ + 2CO$	(0.95)
	$CoNOC_5H_9OCl^+ + H_2 + 2CO$	(0.10)		
	$CoNOP^+ + 2CO$	(0.20)		
$Co(CO)_3NO^+$	$CoCONOC_5H_{10}O^+ + HCl + 2CO$	(0.71)	$CoNOP^+ + 3CO$	(0.88)
	$CoNOC_5H_9OCl^+ + H_2 + 3CO$	(0.16)	$CoCONOP^+ + 2CO$	(0.12)
	$CoNOP^+ + 3CO$	(0.13)		

Table 15

Reaction Products Observed for 1-Bromo-n-Chloro-Alkanes with Co^+-Containing Ions

	P (parent)					
Reactant						
Co^+	$CoCl^+ + C_2H_4Br$	(0.11)	$CoC_3H_4^+ + HCl + HBr$	(0.60)	$CoC_4H_6^+ + HBr + HCl$	(0.10)
	$C_2H_4Br^+ + CoCl$	(0.73)	$C_3H_6Br^+ + CoCl$	(0.40)	$C_4H_8Br^+ + CoCl$	(0.17)
	$CoC_2H_4Cl^+ + Br^{\cdot}$	(0.11)			$C_4H_8Cl^+ + CoBr$	(0.73)
	CoP^+	(0.05)				
$CoCO^+$	$C_2H_4Br^+ + CoCl + CO$	(0.35)	$CoC_3H_5Cl^+ + HBr + CO$	(0.42)	$CoC_4H_6^+ + HBr + HCl + CO$	(0.09)
	$CoC_2H_4Cl^+ + Br^{\cdot} + CO$	(0.23)	$CoC_3H_5Br^+ + HCl + CO$	(0.27)	$CoC_4H_7Cl^+ + HBr + CO$	(0.09)
	$CoP^+ + CO$	(0.24)	$CoP^+ + CO$	(0.11)	$CoCOC_4H_7Cl^+ + HBr$	(0.06)
	$CoCOP^+$	(0.18)	$CoCOP^+$	(0.20)	$C_4H_8Br^+ + CoCl + CO$	(0.10)
					$C_4H_8Cl^+ + CoBr + CO$	(0.66)
$Co(CO)_2^+$	$CoP^+ + 2CO$	(0.39)	$CoP^+ + 2CO$	(0.70)	$CoCOC_4H_7Cl^+ + HBr + CO$	(0.59)
	$CoCOP^+ + CO$	(0.61)	$CoCOP^+ + CO$	(0.30)	$CoCOC_4H_7Br^+ + HCl + CO$	(0.41)
$CoNO^+$	N.R.		N.R.		N.R.	
$CoCONO^+$	$CoNOP^+ + CO$	(1.00)	$CoNOC_3H_5Cl^+ + HBr + CO$	(0.33)	N.R.	
			$CoNOP^+ + CO$	(0.67)		
$Co(CO)_2NO^+$	$CoNOP^+ + 2CO$	(0.91)	$CoNOP^+ + 2CO$	(0.96)	$CoNOP^+ + 2CO$	(1.00)
	$CoCONOP^+ + CO$	(0.09)	$CoNOC_3H_4ClBr^+ + H_2 + 2CO$	(0.04)		
$Co(CO)_3NO^+$	$CoCONOP^+ + 2CO$	(1.00)	N.R.		$CoNOP^+ + 3CO$	(1.00)

Table 15 continues

Table 15 continued

Reactant	P (parent)			
				
Co^+	$C_4H_7^+$ + { $CoBr + CH_3Cl$ or $CoCl + CH_3Br$ }	(0.05)	$C_6H_{11}^+$ + { $CoBr + HCl$ or $CoCl + HBr$ }	(0.20)
	$C_5H_9^+$ + { $CoBr + HCl$ or $CoCl + HBr$ }	(0.28)	$CoC_4H_6^+$ + { $C_2H_5Br + HCl$ or $C_2H_5Cl + HBr$ }	(0.15)
	$C_5H_{10}Cl^+ + CoBr$	(0.03)	$C_4H_8Br^+ + C_2H_4 + CoCl$	(0.16)
	$CoC_5H_8^+ + HCl + HBr$	(0.06)	$CoHBr^+ + C_6H_{11}Cl$	(0.15)
	$CoC_3H_5Cl^+ + C_2H_5Br$	(0.31)	$CoC_6H_{10}^+ + HBr + HCl$	(0.20)
	$C_5H_{10}Br^+ + CoCl$	(0.08)	$CoC_4H_7Cl^+ + C_2H_5Br$	(0.05)
	$CoC_3H_5Br^+ + C_2H_5Cl$	(0.11)	$CoC_6H_{11}Cl^+ + HBr$	(0.09)
	m/z 156	(0.04)		
	m/z 159	(0.04)		
$CoCO^+$	$C_5H_{10}Cl^+ + CoBr + CO$	(0.05)	$CoC_6H_{10}^+ + HBr + HCl + CO$	(0.63)
	$C_5H_{10}Br^+ + CoCl + CO$	(0.07)	$CoC_4H_7Cl^+ + C_2H_5Br + CO$	(0.09)
	$CoC_5H_8^+ + HCl + HBr$	(0.06)	$CoC_6H_{11}Cl^+ + HBr + CO$	(0.16)
	$CoC_3H_5Cl^+ + C_2H_5Br + CO$	(0.21)	$CoCOC_6H_{11}Cl^+ + HBr$	(0.12)
	$CoC_5H_9Cl^+ + HBr + CO$	(0.30)		
	$CoC_3H_5Br^+ + C_2H_5Cl + CO$	(0.06)		
	$CoCOC_5H_9Cl^+ + HBr$	(0.09)		
	m/z 156	(0.10)		
	m/z 159	(0.06)		
$Co(CO)_2^+$	$CoC_5H_9Cl^+ + HBr + 2CO$	(0.70)	$CoC_6H_{11}Cl^+ + HBr + 2CO$	(0.62)
	$CoCOC_5H_9Cl^+ + HBr + CO$	(0.30)	$CoCOC_6H_{11}Cl^+ + HBr + CO$	(0.38)
$CoNO^+$	N.R.		N.R.	
$CoCONO^+$	$C_5H_{10}Br^+ + CoNOCl + CO$	(1.00)	N.R.	
$Co(CO)_2NO^+$	$CoNOP^+ + 2CO$	(1.00)	$CoNOP^+ + 2CO$	(1.00)
$Co(CO)_3NO^+$	N.R.		$CoNOP^+ + 3CO$	(1.00)

$Cl\text{-}C^5\text{-}C^4\text{-}C^3\text{-}C^2\text{-}C^1\text{-}OH$

For three of the products listed in Table 14, $CoC_3H_5Cl^+$, $CoC_3H_5OH^+$ and $CoC_2H_2O^+$, the implication of the site of attack is apparent. The $CoC_3H_5Cl^+$ and $CoC_3H_5OH^+$ product ions are formed through metal insertion into the C^2-C^3 and the C^3-C^4 bond respectively. Insertion into the C^2-C^3 bond also leads to the $CoC_2H_2O^+$ product ion, via elimination of C_3H_7Cl followed by H_2 elimination from the resulting $CoC_2H_3OH^+$ ion. It is not apparent how the rest of the products are formed. For example there are two ways of forming the $CoC_4H_6{}^+$ products ion: (1) If $CoC_4H_7Cl^+$ loses HCl to form $CoC_4H_6{}^+$, then the $CoC_4H_6{}^+$ ion follows insertion into the C^1-C^2 bond. In that case CH_3OH and HCl would be the neutrals lost. (2) If $CoC_4H_6{}^+$ is a dehydration product of $CoC_4H_8O^+$, then the ion is formed through metal insertion into the C^4-C^5 bond. In this case CH_3Cl and H_2O would be the neutrals lost. Similar reasoning can be applied in explaining the formation of the other two product ions $CoC_3H_4{}^+$ and $CoC_5H_8{}^+$, observed in the case of Co^+ reacting with 5-chloro-1-pentanol (Table 14).

Similar cases have been encountered for the rest of the haloalcohols and dihaloalkanes studied, whenever product ions are formed via loss of more than one neutral species. For instance in the case of Co^+ reacting with 1-bromo-6-chloro-hexane, the $CoC_4H_6{}^+$ product ion can be formed either from $CoC_4H_7Cl^+$ via loss of HCl or from $CoC_4H_7Br^+$ via loss of HBr. (The other neutral lost would be C_2H_5Br and C_2H_5Cl, respectively.) Similarly, in the formation of the $C_6H_{11}{}^+$ product ion the neutrals lost can be either CoBr and HCl or CoCl and HBr (Table 15).

Thus it is not feasible to analyze the products of the chloroalcohols and bromochloroalkanes (Tables 14 and 15) to obtain an order of preference for the site of insertion as was done for chloroalkanes and alcohols in the previous chapter (Table 10).

Nonetheless the products of the reaction between the Co^+ and these bifunctional organic molecules are related to the reactant molecule. Consider the case of chloroalcohols reacting with Co^+. One possible explanation of the products may reflect the fact that one functional group dominates the chemistry. That is, we may ask: Are the products observed indicative of "alcohol-like" reactions or of "alkyl chloride-like" reactions? A second possibility involves a combination of both. If this is the case, what fraction of the products is due to the alcohol chemistry and is the remaining fraction due to alkyl chloride chemistry?

Take as an example the chemistry of Co^+ with 4-chloro-1-butanol (Table 14). In the organic molecule there are three C-C bonds, one C-OH bond and one C-Cl bond available for metal ion insertion:

$$Cl\text{-}C^4\text{-}C^3\text{-}C^2\text{-}C^1\text{-}OH$$

The $CoC_4H_8O^+$ and the $CoC_2H_2O^+$ product ions are formed through metal insertion into the C^4-Cl and the C^3-C^2 bond respectively. The former can be considered as a product representative of an alkyl chloride reaction while the latter as a product representative of an alcohol reaction. (All three C-C bonds in n-butyl chloride, bonds that correspond to C^4-C^3, C^3-C^2, C^2-C^1 bonds in 4-chloro-1-butanol, are not attacked - Table 10). Comparison of the branching ratios of the products formed through metal insertion into the C^4-Cl and the C^3-C^2 bond of 4-chloro-1-butanol (Table 14) with those of the products formed by metal insertion into the C-Cl bond of n-butyl chloride and into the C^3-C^2

bond of n-butanol (Table 8), leads to the conclusion that 66% of the products observed for the bifunctional compound should be indicative of an "alcohol-like" behavior and 34% of the products indicative of an "alkyl chloride-like" behavior.

On this basis we should be able to predict the fraction of products coming through metal insertion into each bond of the 4-chloro-1-butanol from the fraction of products coming through metal insertion into each bond of the corresponding alcohol and alkyl chloride (1-butanol and n-butyl chloride respectively - Tables 8 and 9), by applying equation (17).

$$\text{Products} = \sum[(0.66 \times F_{ROH}) + (0.34 \times F_{RCl})] \qquad (17)$$

In equation (17), F_{ROH} and F_{RCl} are the fractions of products coming through insertion of Co^+ into each bond of 1-butanol and n-butyl chloride respectively. In Table 16, the observed percentage of products coming from metal insertion into each bond of 4-chloro-1-butanol is compared to the one predicted using equation (17). It can be seen that there is a difference between the predicted and the experimentally observed percentages of the products coming through metal insertion into each bond.

Therefore use of equation (17) does not give a correct picture of the amount of products coming from metal insertion into each bond of the bifunctional organic molecule and consequently it is not possible to predict a correct order of preferred site of attack. Similar analyses for the rest of the series of n-chloro-1-alcohols and 1-bromo-n-chloro-alkanes studied, showed that the observed products between Co^+ and these compounds do *not* follow any trend consistent with an equation similar to (17). Therefore, even though some of the observed products are representative of alkyl chloride and alcohol or alkyl bromide reactions, the percentage of each behavior cannot be estimated. This

Table 16

Predicted Product Distribution for the Reaction of Co^+ with 4-Cl-1-Butanol

$$Cl — C^4 — C^3 — C^2 — C^1 — OH$$

	$Cl — C^4$	$C^3 — C^2$	$C^1 — OH$
F_{RCl} for $n-C_4H_9Cl$	1.00		
F_{ROH} for $n-C_4H_9OH$		0.28	0.51
Product distribution for ClC_4H_8OH predicted by using eq. (17) (adjusted to 100%)	0.39	0.21	0.40
Product distribution observed for ClC_4H_8OH	0.65	0.35	

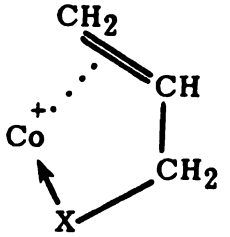
leads to the conclusion that these products are *unique* to the combination of functional groups, i.e., either Cl/OH or Cl/Br and chain length.

One approach that can be used to explain product distributions is based on the stability of the metal-insertion intermediates. Whenever a number of metal-insertion intermediates of the type R_1-M^+-R_2 are possible, those in which the sum of the two M^+-R bond energies is greatest are the more stable and thus appear to be preferentially formed at least in the case of M^+-alkane reactions [83]. For example, in the case of Co^+ reacting with n-pentane, metal insertion into the internal C-C bond is favored over insertion into the terminal C-C bond since:

$$[D°(Co^+\text{-}C_2H_5) + D°(C_2H_5Co^+\text{-}C_3H_7)] > [D°(Co^+\text{-}CH_3) + D°(CH_3Co^+\text{-}C_4H_9)] \quad (18)$$

Note that $D(Co^+\text{-}C_nH_{2n+1})$ increases with increasing n. Is the same trend observed when two functional groups are present in the alkyl chain, i.e., in the case of chloroalcohols and bromochloroalkanes? For example, is metal insertion into the internal C-C bond still favored over insertion into the terminal C-C bond in the case of 5-chloro-1-pentanol and 1-bromo-5-chloro-pentane, where two functional groups are attached at the end of the alkyl chain? That should be true assuming a relation between the bondstrengths of the bonds formed in the reaction intermediates, similar to the one described by equation (18), unless there are some secondary interactions between the metal ion center and the functional groups in the reaction intermediates. Some insights into the structure of the metal insertion intermediates can be provided by the β-H shift trends observed in the results in Tables 14 and 15.

The possible metal-insertion intermediates for some of the bifunctional organic molecules studied (those with five and six carbon atoms chain length), along with the possible β-H shifts leading to observed products, are presented in Table 17. It can be seen that in the case of 5-chloro-1-pentanol a β-H shift from the $-C_3H_6OH$ group is favored over that from the $-C_2H_4Cl$ group (intermediate 39), while a β-H shift from the $-C_3H_6Cl$ group is favored over that from the $-C_2H_4OH$ group (intermediate 40). Similarly in the case of 1-bromo-5-chloro-pentane in both intermediates 41 and 42, the H that shifts is provided by the $-C_3H_6X$ group (X = Br, Cl). Since H-shift occurs from the largest alkyl group carrying the functional group, the above observed behavior is consistent with the trend observed in the case of alkanes. Another possible explanation of this behavior is the stability of the final product formed:

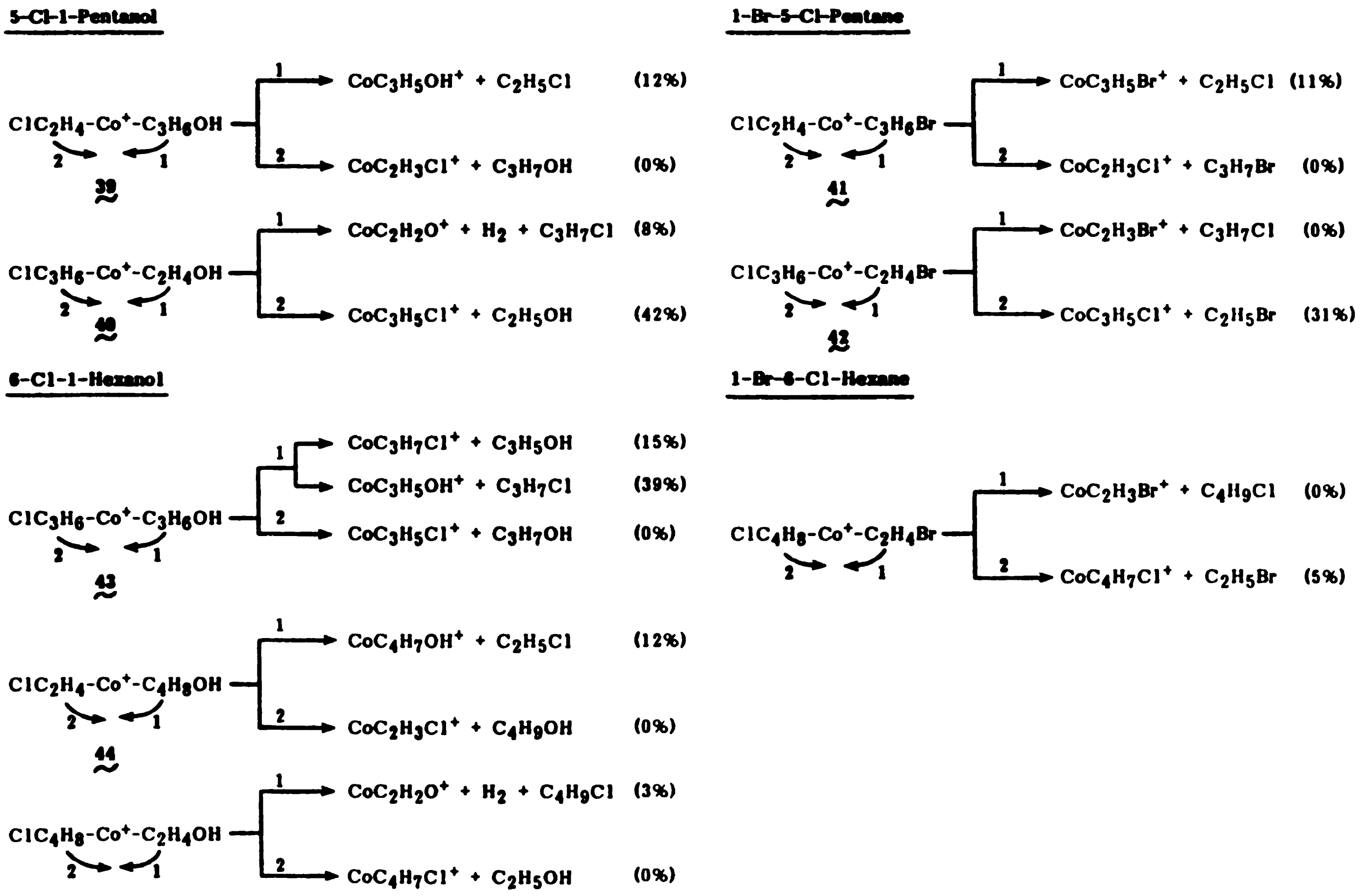


X = OH,Cl,Br

Formation of the most stable metal-insertion intermediate is not apparent in the case of Co^+ reacting with 6-chloro-1-hexanol, where the H-shift from the hydroxy-alkyl group is always preferred over that from the chloro-alkyl group, regardless of the chain length (Table 17). In this case, we probably have a metal-chloride interaction following Co^+ insertion into the various skeletal C-C bonds, that moves the β-H atoms of the chloroalkyl group away from the metal making them inaccessible to shift.

Table 17

Metal Insertion Intermediates and β-H Shift Trends for Some Bifunctional Molecules



5-Cl-1-Pentanol

39: $ClC_2H_4\text{-}Co^+\text{-}C_3H_6OH \xrightarrow{1} CoC_3H_5OH^+ + C_2H_5Cl$ (12%)

39: $ClC_2H_4\text{-}Co^+\text{-}C_3H_6OH \xrightarrow{2} CoC_2H_3Cl^+ + C_3H_7OH$ (0%)

40: $ClC_3H_6\text{-}Co^+\text{-}C_2H_4OH \xrightarrow{1} CoC_2H_2O^+ + H_2 + C_3H_7Cl$ (8%)

40: $ClC_3H_6\text{-}Co^+\text{-}C_2H_4OH \xrightarrow{2} CoC_3H_5Cl^+ + C_2H_5OH$ (42%)

6-Cl-1-Hexanol

43: $ClC_3H_6\text{-}Co^+\text{-}C_3H_6OH \xrightarrow{1} CoC_3H_7Cl^+ + C_3H_5OH$ (15%)

43: $ClC_3H_6\text{-}Co^+\text{-}C_3H_6OH \xrightarrow{1} CoC_3H_5OH^+ + C_3H_7Cl$ (39%)

43: $ClC_3H_6\text{-}Co^+\text{-}C_3H_6OH \xrightarrow{2} CoC_3H_5Cl^+ + C_3H_7OH$ (0%)

44: $ClC_2H_4\text{-}Co^+\text{-}C_4H_8OH \xrightarrow{1} CoC_4H_7OH^+ + C_2H_5Cl$ (12%)

44: $ClC_2H_4\text{-}Co^+\text{-}C_4H_8OH \xrightarrow{2} CoC_2H_3Cl^+ + C_4H_9OH$ (0%)

$ClC_4H_8\text{-}Co^+\text{-}C_2H_4OH \xrightarrow{1} CoC_2H_2O^+ + H_2 + C_4H_9Cl$ (3%)

$ClC_4H_8\text{-}Co^+\text{-}C_2H_4OH \xrightarrow{2} CoC_4H_7Cl^+ + C_2H_5OH$ (0%)

1-Br-5-Cl-Pentane

41: $ClC_2H_4\text{-}Co^+\text{-}C_3H_6Br \xrightarrow{1} CoC_3H_5Br^+ + C_2H_5Cl$ (11%)

41: $ClC_2H_4\text{-}Co^+\text{-}C_3H_6Br \xrightarrow{2} CoC_2H_3Cl^+ + C_3H_7Br$ (0%)

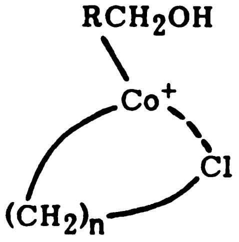
42: $ClC_3H_6\text{-}Co^+\text{-}C_2H_4Br \xrightarrow{1} CoC_2H_3Br^+ + C_3H_7Cl$ (0%)

42: $ClC_3H_6\text{-}Co^+\text{-}C_2H_4Br \xrightarrow{2} CoC_3H_5Cl^+ + C_2H_5Br$ (31%)

1-Br-6-Cl-Hexane

$ClC_4H_8\text{-}Co^+\text{-}C_2H_4Br \xrightarrow{1} CoC_2H_3Br^+ + C_4H_9Cl$ (0%)

$ClC_4H_8\text{-}Co^+\text{-}C_2H_4Br \xrightarrow{2} CoC_4H_7Cl^+ + C_2H_5Br$ (5%)



This explanation has been used previously to explain the failure of a β-H shift to occur [26,36].

In the case of intermediates 43 and 44, formation of a five- or a six-membered ring intermediate via a Co$^+$-O interaction is possible, which weakens the O-H bond, facilitating the H-shift. Therefore it is the hydroxy-H, a δ- or an ε-hydrogen, which shifts onto the metal via a cyclic intermediate - a process similar to the one shown in Scheme VII for n-hexanol.

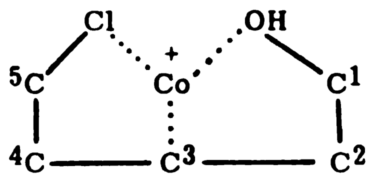
Thus an explanation of the product distributions based on a consistent approach of the stability of the metal-insertion intermediates cannot be used for the series of chloroalcohols and bromochloroalkanes. This is due to the apparent interaction of Co$^+$ with one or both functional groups in the reaction intermediates.

Another approach used to explain product distributions reflects involvement of both functional groups in the reaction intermediates, where the interaction between the Co$^+$ and the two functional groups has a dominant effect on the metal insertion step that follows. That is, the initial intermediate geometry is probably directing the metal ion to insert into certain skeletal C-C bonds.

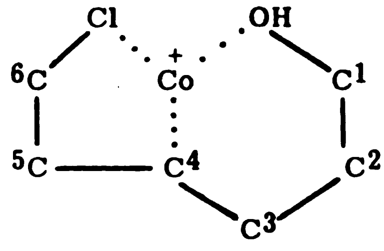
Even though the ordering for site of metal insertion is not available (because the mechanistic sequence under which some of the products are formed is not known), the bond into which Co$^+$ insertion occurs most frequently - leading to the largest fraction of products - can be deduced for the series of chloroalcohols studied. In Table 18, the most "preferred" bond for metal insertion (labeled ①) is indicated for the series of chloroalcohols studied.

Table 18 shows that for small chain length ($n < 5$), the bond that is most susceptible to attack is the C-Cl bond. As the chain length increases, metal ion insertion into internal C-C bonds becomes preferred over insertion into the C-Cl bond. This can be explained by using a mechanistic model similar to the one proposed in Chapter 4 for the reactions of Co$^+$ with n-alcohols, i.e., metal-carbon atom interactions occur via cyclic intermediates leading to metal ion insertion into specific C-C bonds.

In the case of 5-chloro-1-pentanol and 6-chloro-1-hexanol, the reaction model involves metal ion interaction with both functional groups simultaneously and the formation of the bicyclic intermediates **45** and **46** respectively.



45

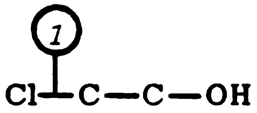


46

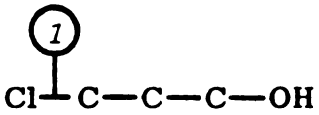
The resulting interaction between Co$^+$ and a particular C atom (C^3,C^4) weakens the C-C bonds containing this C atom, making them susceptible to attack. Thus it can be explained why the C^2-C^3 bond in the 5-chloro-1-pentanol and the C^3-C^4 bond in the 6-chloro-1-hexanol is the most "preferred" site of attack

Table 18

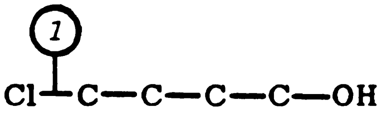
Most Preferred Site for Metal Insertion for the n-Cl-1-Alcohols[a]



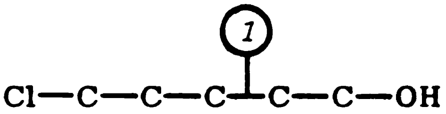
$$\mathrm{Cl}\overset{\textcircled{1}}{\vert}\mathrm{C-C-OH}$$



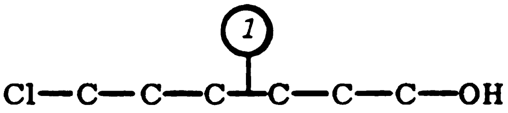
$$\mathrm{Cl}\overset{\textcircled{1}}{\vert}\mathrm{C-C-C-OH}$$



$$\mathrm{Cl}\overset{\textcircled{1}}{\vert}\mathrm{C-C-C-C-OH}$$



$$\mathrm{Cl-C-C-C}\overset{\textcircled{1}}{\vert}\mathrm{C-C-OH}$$



$$\mathrm{Cl-C-C-C}\overset{\textcircled{1}}{\vert}\mathrm{C-C-C-OH}$$

---

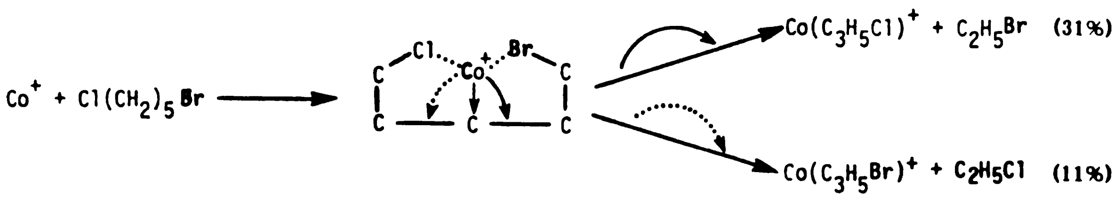
[a] Whenever a cobalt-1, n-alkadiene product ion is formed, it is assumed that metal insertion into the C-Cl bond occurs first, leading to HCl elimination. Then metal insertion into the C-OH bond follows, leading to H_2O elimination and formation of the $Co(1,n\text{-alkadiene})^+$ complex.

(Table 18). Therefore it can be seen that the initial intermediate geometry has a directing effect on the most "preferred" site of metal insertion.

These bicyclic intermediates can be also used to explain why the C-C bonds that are α - with respect to each functional group are *not* attacked, e.g., the C^1-C^2 bond in the case of intermediate 45 and C^1-C^2, C^5-C^6 bonds in the intermediate 46. The only exception is the C^4-C^5 bond in intermediate 45, where insertion into this C-C bond leads eventually to the very stable $CoC_4H_6^+$.

In the series of 1-bromo-n-chloroalkanes there is more than one bond than can be labeled ① , i.e., the most "preferred" bond, due to a number of ambiguities concerning the formation of product ions. The suggested mechanistic model involving bicyclic intermediates can be used though, to account for some of the major products in the chemistry of Co^+ with 1-bromo-5-chloro-pentane (Scheme XI).

Scheme XI



Some characteristic products are observed for the series of 1-bromo-n-chloroalkanes: **(1)** The formation of alkyl ions for large alkyl chains (n > 4), the $C_4H_7^+$ and $C_5H_9^+$ for 1-bromo-5-chloro-pentane and the $C_6H_{11}^+$ for 1-bromo-6-chloro-hexane. Similar formation of alkyl cations has been previously observed for the series of chloroalkanes (Tables 8 and 9). (2) The chloride and bromide abstraction reactions observed throughout the series of 1-bromo-n-chloroalkanes with the exception of 1-bromo-6-chloro-hexane. Note that, when Co^+ reacts by halide abstraction, the resulting product $C_nH_{2n}X^+$ ($n = 2$-5, $X = Br, Cl$) could be a cyclic halonium ion. In the case of 1-bromo-6-chloro-hexane we do not observe the $C_6H_{12}Br^+$ ion, but the $C_4H_8Br^+$ bromonium ion is observed instead. The failure to observe $C_6H_{12}Br^+$ may be due to rapid fragmentation following its formation, leading to the stable cyclic $C_4H_8Br^+$ ions:

$$Co^+ + ClC_6H_{12}Br \xrightarrow{-CoCl} [C_6H_{12}Br^+]^* \xrightarrow{-C_2H_4} C_4H_8Br^+$$

II. The Chemistry of CoL_x^+ with n-Chloro-1-Alcohols and 1-Bromo-n-Chloro-Alkanes

Most of the current interest in the field of gas phase organometallic chemistry today is the chemistry of the bare metal ion with various organic molecules. Electron impact on metal-containing compounds generates metal centers with a number of various ligands attached. In the case of $Co(CO)_3NO$ (at low pressures), these ions are the $Co(CO)_x^+$ ($x = 1,2$) and the $Co(CO)_yNO^+$ ($y = 0$-3). The chemistry of these ions with the series of chloroalcohols and bromochloroalkanes is presented in Tables 14 and 15 respectively. Evaluation of these results and identification of the changes in chemistry exhibited by the metal center as the number of attached ligands changes and/or as the chain length of the organic molecule increases, can supply valuable information on the "ligand effects".

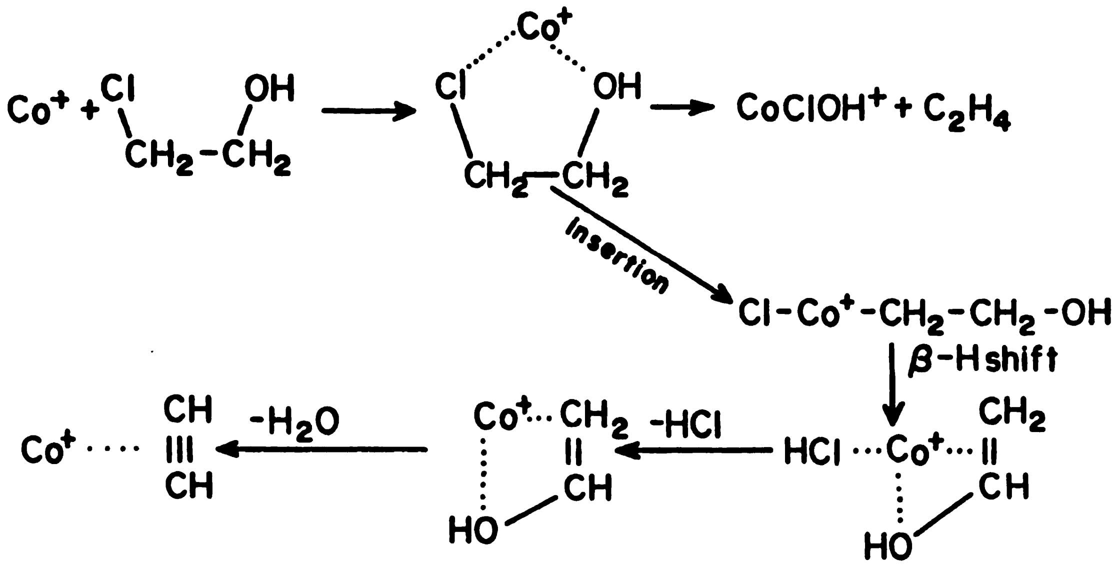
n-Chloro-1-Alcohols

All of the metal-containing ions derived from $Co(CO)_3NO$ exhibit a rich-chemistry with all the n-chloro-1-alcohols studied. In general, the chemistry of the cobalt-containing ions with bifunctional organic molecules is much richer than that with monofunctional molecules. This is because in the former case two groups can bond to the metal, which results in more energy released in the intermediate complex than in the latter case. More specifically in the case of n-chloro-1-alcohols we observe the following: (1) The organic rearrangement reactions observed for $CoCO^+$ are similar to those observed for Co^+ [20,26,34,35]. Therefore, the bare metal ion is not the only ionic species that forms a large variety of products. For example in the case of Co^+ and $CoCO^+$ reacting with 2-chloroethanol (P), the observed products are (Table 14):

$$
\begin{array}{lll}
Co^+ + ClC_2H_4OH & \longrightarrow C_2H_4OH^+ + CoCl & (27\%) \\
 & \longrightarrow CoH_2O^+ + C_2H_3Cl & (2\%) \\
 & \longrightarrow CoC_2H_2{}^+ + HCl + H_2O & (8\%) \\
 & \longrightarrow CoC_2H_3OH^+ + HCl & (22\%) \\
 & \longrightarrow CoClOH^+ + C_2H_4 & (41\%)
\end{array}
$$

$$
\begin{array}{lll}
CoCO^+ + ClC_2H_4OH & \longrightarrow C_2H_4OH^+ + CoCl + CO & (8\%) \\
 & \longrightarrow CoCOH_2O^+ + C_2H_3Cl & (2\%) \\
 & \longrightarrow CoC_2H_3OH^+ + HCl + CO & (64\%) \\
 & \longrightarrow CoC_2H_4OH^+ + Cl\cdot + CO & (4\%) \\
 & \longrightarrow CoCOC_2H_3OH^+ + HCl & (4\%) \\
 & \longrightarrow \left.\begin{array}{l} CoCOClOH^+ + C_2H_4 \\ \text{and/or} \\ CoP^+ + CO \end{array}\right\} & (9\%) \\
 & \longrightarrow CoCOP^+ & (5\%) \\
 & \longrightarrow m/z\ 133 & (4\%)
\end{array}
$$

Co^+ alone reacts with 2-chloroethanol by metal insertion into the C-Cl bond leading to 57% of the products ($C_2H_4OH^+$, $CoC_2H_3OH^+$ and $CoC_2H_2^+$), and by oxidative addition to form $CoClOH^+$ (41%).

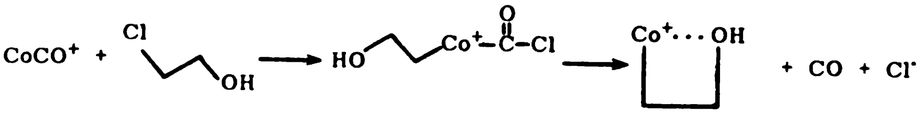


Metal insertion into the C-OH bond accounts only for 2% of the products.

$CoCO^+$ appears to react by metal insertion into the C-Cl or the C-OH bonds and also by a cyclic intermediate. Both Co^+ and $CoCO^+$ react by chloride abstraction, leading to the $C_2H_4OH^+$ product ion - a reaction usually observed for chloroalkanes and which is *only* observed for 2-chloroethanol among the chloroalcohols studied.

It is only the $CoCO^+$ ion though, that reacts with 2-chloroethanol inducing loss of $Cl^{\bullet}$ with concurrent CO elimination. Thus it appears that $CoCO^+$

insertion occurs instead of that of Co^+ (active participation of CO), leading to Cl' loss (reaction (26)).

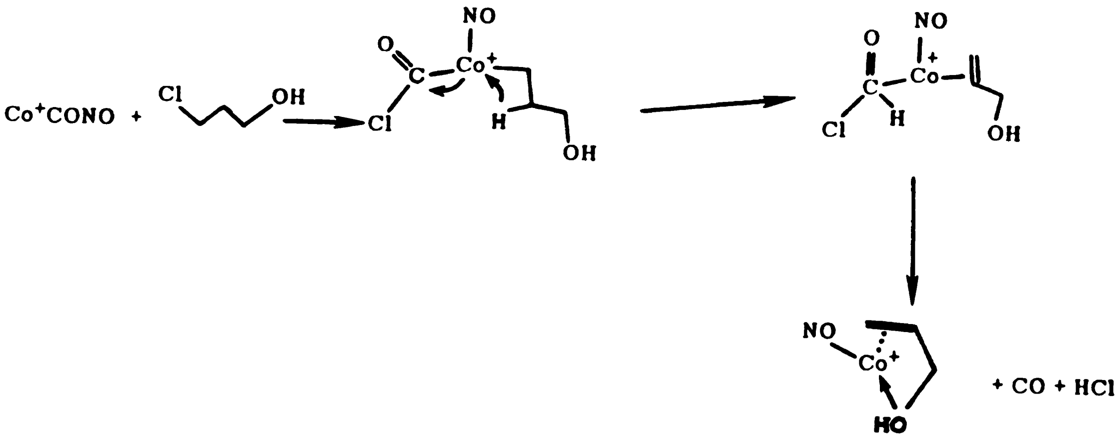


(26)

As the alkyl chain length of the chloroalcohols increases (n $\geq$ 4), metal ion insertion into internal C-C bonds also occurs. Insertion into the bonds containing the functional group (C-Cl, C-OH) becomes less dominant - a behavior similar to that observed for the bare metal ion.

The reactions of $Co(CO)_2^+$ with the series of chloroalcohols resemble those of $CoCO^+$ with the number of reactions reduced for the $Co(CO)_2^+$ ion. Ligand substitution reactions in which one or two CO's are displaced by the organic molecule become more dominant in the case of $Co(CO)_2^+$ ion. (2) The presence of an NO ligand deactivates the metal center [14,20] and thus no products are observed for the $CoNO^+$ ion with the series of chloroalcohols studied, with the exception of 2-chloroethanol where the direct attachment product ($CoNOP^+$) is observed (Table 14). (3) As the number of ligands present on the metal center increases, ligand substitution reactions become more of a dominant process, but to a smaller degree compared to the one observed for the corresponding monofunctional organic molecules of alcohols and chloroalkanes (Chapter 4).

There are a number of processes in which there is evidence for direct involvement of the ligand in the overall process. An example of a "CO participation" reaction is: $CoNO^+$ does not react with 3-chloro-1-propanol, while $CoCONO^+$ induces HCl elimination. Since the reaction is only observed with concurrent CO elimination, this may be an evidence for $CoCO^+$ insertion into the C-Cl bond, i.e.,



(27)

Metal insertion into internal C-C bonds is observed for the $Co(CO)_{2,3}NO^+$ ions, but it is a minor pathway. For example, formation of a metal-methanol complex is observed for the $Co(CO)_{2,3}NO^+$ ions reacting with 4-chloro-1-butanol, via a mechanism involving insertion of the CoCO group into the C-C(OH) bond followed by a β-H shift, leaving a methanol complex (Chapter 3).

Another reaction observed for the $Co(CO)_{2,3}NO^+$ ions is the elimination of H_2 with concurrent loss of two or three CO's in the case of $Co(CO)_2NO^+$ and $Co(CO)_3NO^+$ respectively. This reaction apparently proceeds through a series of ligand losses followed by metal insertion into a C-H bond. The possibility of a metal insertion into the O-H bond leading to an intermediate similar to 38 (reaction (25)), followed by a β-H shift leading to elimination of H_2 and CO (maybe in the form of H_2CO), has to be considered as well.

1-Bromo-n-Chloro-Alkanes

In the series of 1-bromo-n-chloroalkanes, $CoCO^+$ reacts to form the same products as Co^+ does. For small alkyl chain lengths, $CoCO^+$ appears to react by metal insertion into the C-Cl and C-Br bonds. In most cases, the CO is also lost in the reaction. As the alkyl chain length increases (n > 4) metal ion insertion into internal C-C bonds is observed, as in the case of chloroalcohols.

The $Co(CO)_2^+$ ion reacts by ligand displacement reactions in which one or two CO's are displaced by the organic molecule, but as the chain length increases metal insertion into the polar C-X (X = Br, Cl) bonds leading to HX elimination, becomes the dominant pathway.

In contrast with the $CoCO^+$ ion, no products are observed for the $CoNO^+$ ion reacting with all the bromochloroalkanes studied. $CoCONO^+$ ion is not as reactive either, with the exception of 1-bromo-3-chloro-propane. In this case, $CoCONO^+$ induces HBr elimination along with loss of the CO group through $CoCO^+$ insertion into the C-Br bond - a mechanism similar to the one observed for 3-chloro-1-propanol in reaction (27).

The chemistry of $Co(CO)_2NO^+$ and $Co(CO)_3NO^+$ is dominated by ligand substitution reactions throughout the series of bromochloroalkanes. Unlike the case of chloroalcohols, metal insertion into C-X or C-C bonds is not observed, probably due to the lack of sufficient energy in the reaction intermediate complex where the two functional groups can interact with the metal. (The metal interacts more strongly with an hydroxy group than with an halide group).

CHAPTER 6

SUMMARY AND CONCLUSIONS

The chemistry of the cobalt-containing ions $Co(CO)_x^+$ and $Co(CO)_xNO^+$ with 1-halobutanes is similar to that of smaller haloalkanes. The main difference between halobutanes and smaller haloalkanes which have been previously studied is that, when such a molecule contains a four-carbon chain, HX elimination can be followed by H_2 elimination to form a metal-butadiene complex. The 1,4-bisubstituted n-butanes exhibit an unexpected chemistry with metal ions. Metal insertion into the central C-C bond halobutanols is a major pathway, while $CoCO^+$ prefers insertion into the C-C(OH) bond. The proton affinity rule along with collision-induced dissociation (CID) analysis proved to be useful in providing insights into mechanisms and ionic product structures. CID analysis can be difficult to interpret in organometallic systems because of the ease with which collision-induced decomposition of ligands can occur.

In the study of the chemistry of cobalt-containing ions with a series of straight chain alkyl chlorides and alcohols, increases in chain length lead to a rich chemistry in both cases. Metal ions such as Co^+ react with longer chain n-alkyl chlorides and n-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 n-alcohols. This is consistent with the proton affinity rule 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 small alcohols and alkyl chlorides ($n < 4$).

Long chain alkyl chlorides exhibit some similarities with alkanes concerning the ordering 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 5 or 6-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 energy for Co^+ and alkyl chlories is less than that for alcohols, we do not see the complexation / 5-6 membered ring intermediate process playing as important a role for the chloroalkanes. When complexation of Co^+ with the chlorine atom of an alkyl chloride occurs, metal insertion into the C-Cl bond occurs, favored by the strong Co^+-Cl bond energy [36].

The reactions of $CoCO^+$ and $Co(CO)_2{}^+$ with the series of alcohols and chloroalkanes resemble those of Co^+, with the number of reactions reduced for the $Co(CO)_2{}^+$ ion. The reactions of the other $CoL_x{}^+$ ions with these compounds are dominated by ligand substitution reactions.

Some of the reaction products of Co^+ with a series of n-chloro-1-alcohols and 1-bromo-n-chloroalkanes are seen only with particular combinations of functional groups, i.e., either Cl/OH or Cl/Br and chain length. Even though some of the products are representative of alkyl chloride and alcohol or alkyl bromide reactions, the percentage of each reaction type cannot be estimated. Thus, prediction of the reaction products of Co^+ with similar bifunctional compounds is not feasible at this time.

An interaction between the metal ion and the two functional groups occuring in the reaction intermediate, has a "directing" effect on the metal insertion step that follows. A mechanistic model, similar to the one used for alcohols, involving (bi)cyclic intermediates, is used to account for the major products observed. The model also explains why metal insertion into internal C–C bonds is preferred over insertion into the C-Cl bond as the chain length increases.

As the number of ligands present on the metal center increases, ligand substitution reactions become the dominant process in the case of bromochloroalkanes. Unlike the bromochloroalkanes, metal insertion into C-X or internal C-C bonds is observed for the CoL_x^+ ions with the series of chloroalcohols, probably due to the additional energy in the reaction intermediate complex contributed by the strong initial Co^+······OH interaction.

In terms of the analytical utility of metal ions as CI reagents in mass spectrometry, these results are "interesting". In the work done to date, it is shown that metal ions such as Co^+ react in specific ways with organic molecules. For example, Co^+ prefers to attack at the polar bond in small monofunctional molecules, except in the anomalous case of primary amines. Thus, small n-alkyl chlorides and n-alcohols react to give metal–olefin complexes through HCl and H_2O elimination respectively. As shown in this dissertation, longer chain n-alkyl chlorides and n-alcohols ($n > 5$) do not exhibit the same behavior.

Nevertheless generation of the following rules for the prediction of the Co^+-CI mass spectrum for both n-alcohols and n-alkyl chlorides is possible:

(1) Ligand displacement reactions, leading to the series of CoP^+, $CoCOP^+$, $CoNOP^+$ and $CoCONOP^+$ adduct ions, provide molecular weight information for the organic molecules.

(2) Observation of the CoP^+ adduct ion along with the $Co(P-18)^+$ ion is an indication of a small n-alcohol with a chain length of less than five carbon atoms ($n < 5$).

(3) Formation of complexes between the cobalt ion and small olefins resulting from metal insertion into internal C-C bonds, may be indicative of an alcohol or of an alkyl chloride with a chain length of more than four carbon atoms ($n > 4$).

(4) Observation of an alkyl cation or a series of alkyl cations, is characteristic of an alkyl chloride, with the largest alkyl cation being indicative of the size of the alkyl chain (for $n \leq 7$).

Thus if the highest m/z alkyl ion observed is $C_7H_{15}^+$, there is an indication of an heptyl group attached to the functional group. Note that for small alkyl chlorides ($n < 6$), the presence of the corresponding metal-olefin complex gives an additional indication of the chain size.

In bifunctional compounds where we have neighboring functional groups, the products observed in Co^+-CI are unique to their combination (e.g., the formation of $CoClOH^+$ in the case of Co^+ with 2-chloroethanol - Chapter 5). When the two functional groups are far removed in the molecule, products representative of both groups can be observed [3]. In a recent report [23] the reaction products for substituted butanones and carboxylic acids were predicted based upon the known chemistry of each functional group.

A similar prediction of the reaction products for the series of chloroalcohols and bromochloroalkanes is not possible, due to the interaction between the metal ion and both functional groups in the reaction intermediates.

In general, for multifunctional compounds where two or more functional groups can interact simultaneously with the metal ion (as in our case where a straight aliphatic chain connects the two functional groups), we cannot generate rules for the prediction of the Co^+-CI mass spectrum. If this interaction is geometrically restricted (e.g., in the case of 3-substituted butanones [23]), generation of such rules and prediction of the Co^+-CI mass spectrum is possible.

Thus a rule-based system for Co^+-CI mass spectral interpretation is not feasible for the series of chloroalcohols and bromochloroalkanes studied. Nevertheless, information about the molecular weight and one of the functional groups can be supplied by the Co^+-CI mass spectra. The former is obtained from the ligand displacement reactions and the CoP^+, $CoCOP^+$, $CoNOP^+$ adducts while the latter is obtained from the series of $Co(P-HX)^+$, $CoCO(P-HX)^+$ and $CoNO(P-HX)^+$ ions observed, where X = Cl and Br for the case of chloroalcohols and bromochloroalkanes respectively.

APPENDIX A.

Table 19

Pertinent Proton Affinities

Compound	PA (kcal/mole)	Reference
H_2	101	95
CO	139.0	96
CH_4	128	97
C_2H_2	152	98
C_2H_4	160	98
C_3H_6	179	99,100
n-C_4H_8	183	101
HF	112	102
HCl	141 ± 3	97
HBr	140 ± 3	97
H_2O	173.0	103
NH_3	205.0	103
CH_3F	151	104
CH_3Cl	160	104
CH_3Br	163	104
CH_3OH	184.9	103
C_2H_5F	163	104
C_2H_5Cl	167	104
C_2H_5Br	170	104

Table 19 continues

Table 19 continued

C_2H_5OH	190.3	103
CH_2O	165 ± 3	105
	177.2	103
CH_3CHO	188.9	103
CH_2CO	201 ± 2	106

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89. Since Co^+ reacts with i-propanol by hydroxide abstraction leading to formation of the i-propyl cation, a lower limit can be deduced, ΔH°$_f$ (CoOH) < 27.4 kcal/mole. 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 n-propanol (Table 8), an upper bound is suggested, D(Co^0-OH) < 99.1 kcal/mol.

90. For example the loss of propane is approximately 18 kcal/mol more exothermic than the loss of ethane [80].

91. 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 [16]. A lower limit on the cobalt-butadiene bond strength, D(Co^+-C_4H_6) > 43.3 kcal/mol has been also reported [34,35].

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