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METAL ION CHEMICAL IONIZATION — THE GAS PHASE
CHEMISTRY OF COBALT CONTAINING IONS

By

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A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1984

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

This is also dedicated to my undergraduate
advisor, the late Dr. Al Steyermark.

ACKNOWLEDGEMENTS

I would like to thank Dr. John Allison for being my advisor the past years. I have learned much from him, both about chemistry and about people.

Thanks goes to Mike Nowak for the help on purifying the substituted acids. Also for being a friend. Thanks to all the people associated with the Aromatics and Free Radicals, these people know how to make softball enjoyable.

I want to give special thanks to my friends from back home. Dave Deininger, whose letters and phone calls always were good for a laugh or two around here. I don't know anyone else who has such strange taste in music. A very special thank-you goes to Diane Siedlecki, one person who always believed in me, even at times when I didn't believe in myself. Whenever I found myself needing to talk to someone she was there. I know that in her I will always have a friend.

I'd like to thank all the support personnel in the electronics, machine and glassblowing shops, without their assistance the ICR and myself would not be where we are today.

ABSTRACT

Metal Ion Chemical Ionization — The Gas Phase Chemistry of Cobalt Containing Ions

The ion/molecule reactions of Co^+ with thiols, butanone, butenone, carboxylic acids, allylic compounds and 2-chloro- and 2-bromoethanols are reported. Primarily, Co^+ reacts with thiols via the metal insertion/ β -H atom shift/competitive ligand loss mechanism that has been used previously to explain the chemistry of gaseous transition metal ions with organic molecules containing other functional groups. With ketones, Co^+ initially attacks at the carbonyl oxygen from which insertion into either C-CO bond may occur, followed by alkyl or β -H atom shifts. In carboxylic acids, the Co^+ reaction products are indicative of metal insertion into either the C-CO or the C-OH bond as the first step, with insertion into the C-OH bond predominating. Co^+ prefers to attack at the substituted group of the allylic compounds; no reactions typical of olefins were observed. In the chemistry of Co^+ with 2-chloroethanol attack at the halides occurs to eliminate HCl. Also observed is the elimination

of ethene which is explained through the formation of a five-membered ring intermediate. Similar reactions are observed in 2-bromoethanol.

Also investigated was the ability to predict reaction products of bifunctional organic compounds based upon the known chemistry of each functional group. The ability to predict products varied from 0% for 2-bromopropanoic acid to 100% for other substituted acids and butanones. From the branching ratios the following trend for site of attack by Co^+ is suggested:

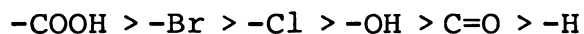


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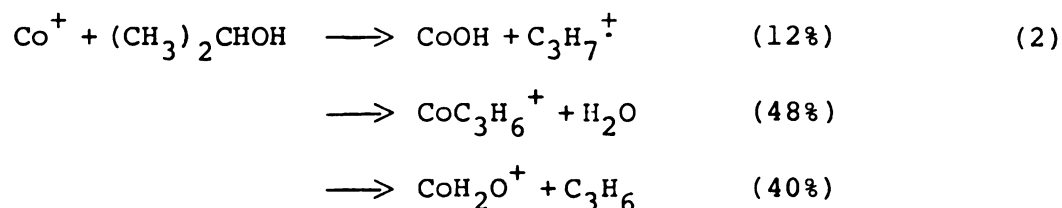
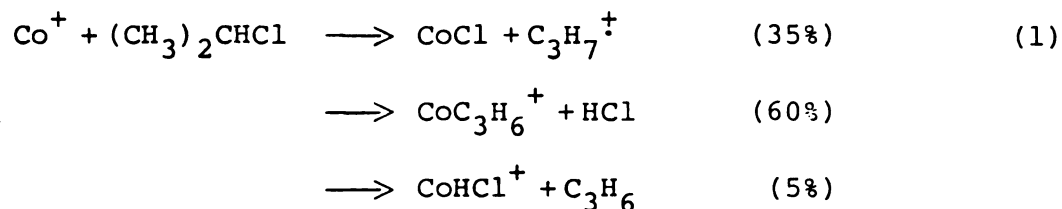
CHAPTER 1

INTRODUCTION

In the past several years, a substantial number of reports have appeared concerning the gas phase chemistry of metal and metal-containing ions with a variety of organic molecules [1,2]. Using Ion Cyclotron Resonance Mass Spectrometry [1a,1b], Fourier Transform Mass Spectrometry (FTMS) [1c], and ion beam techniques [1d] to study ion/molecule reactions in various organometallic systems, a substantial database on the chemistry of metal and metal-containing ions with organic molecules containing various functional groups is now available. One aspect of this work is the development of metal ions as Chemical Ionization (CI) reagents in mass spectrometric analysis [3,4].

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. This dissertation will first deal with the gas phase chemistry of the base Cobalt +1 ion and ions derived from electron impact upon $\text{Co}(\text{CO})_3\text{NO}$ with thiols, butanone, butenone, and unsubstituted carboxylic acids.

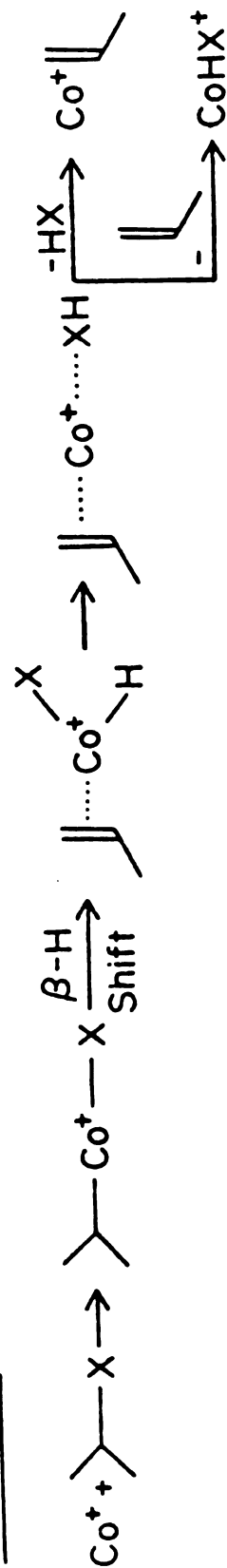
The first compounds that were studied in such experiments were alkyl halides and alcohols [5]. In the presence of Co^+ , 2-chloropropane and 2-propanol react as follows:



These reactions can be explained through a common mechanism (Scheme I). The metal ion inserts into the C-X ($\text{X}=\text{Cl}, \text{OH}$) bond, followed by either a charge transfer process to form C_3H_7^+ , or a β -H atom shift to the metal center to give the $\text{Co}(\text{HX})(\text{olefin})^+$ complex. Next the HX and olefin ligands compete for sites on the metal in a competitive ligand loss process.

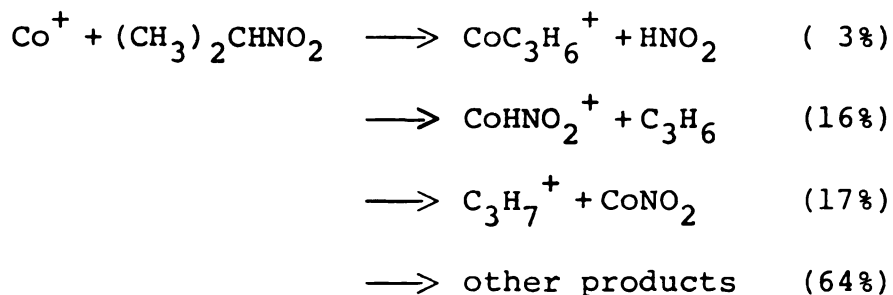
Other halides and alcohols have also been observed to react like 2-chloro-propane and 2-propanol. The Co^+ ion reacts with ethyl iodide via insertion into the C-I bond followed by either a bond cleavage to give CoI^+ (11%), or a β -H atom shift to give $(\text{ethene})\text{Co}^+(\text{HI})$ complex which then undergoes competitive ligand loss to give CoHI^+ (11%)

Scheme I



and CoC_2H_4^+ (78%). Co^+ reacts with ethanol via the same mechanism to give CoH_2O^+ (13%) and CoC_2H_4^+ (87%).

One area of research in our laboratory deals with the chemistry of metal ions with nitrogen containing compounds. The bare cobalt ion, Co^+ , shows a rich chemistry with 2-nitropropane. There are three reaction products that are formed via the same mechanism as the chloride and alcohol to give the observed products [6]:



From the reactions of Co^+ with these three compounds, one would conclude that Co^+ would insert into the polar C-X bond in all compounds, therefore making prediction of metal ion-CI spectra relatively straightforward. For example, using the mechanism in Scheme I, one might predict that 2-aminopropane would react with Co^+ to give the products CoNH_3^+ and/or CoC_3H_6^+ . This, however, is not observed. For primary amines, insertion of Co^+ into the N-H, C-H, and C-C bonds dominates the chemistry [7], resulting in H_2 and CH_4 elimination and the formation of $\text{C}_3\text{H}_8\text{N}^+$ (with the loss of the neutral CoH).

Although the sites of attack in amines by cobalt varies from the molecules containing other polar functional groups, the same general mechanism — metal ion insertion/ β -H atom shift/competitive ligand loss — can still be used to explain the products. This general mechanism can be used to explain approximately 90% of all products in 2-propylamine. The failure of Co^+ to insert into the C-NH₂ bond has been proposed to be due to the weak $\text{Co}^+\text{-NH}_2$ bond that would be formed. This is just one example where Co^+ does not insert into the polar C-X bond. In compounds containing no polar bonds (alkanes and alkenes), the chemistry of the Co^+ is dominated also by the metal ion insertion into the C-H and C-C bonds as the first mechanistic step [8,9].

From these examples, it is illustrated that the ion/molecule reaction products of species such as Co^+ with organic molecules could be predicted if the initial sites of attack are known. It is apparent that Co^+ prefers to attack at the polar bond in small monofunctional molecules, except in the anomalous case of primary amines. Basic studies involving molecules representative of various functional groups continue to be a major area of research for gas phase metal ion chemists.

Most compounds being analyzed by mass spectrometry today are not simple monofunctional molecules, but rather complicated multifunctional molecules. To date, only three reports [4,10,11] have dealt with the ion/molecule

reactions of Co^+ with bifunctional compounds to any extent. In the first report, (based upon some of the work in this dissertation), the chemistry of gaseous transition metal ions with molecules containing two functional groups on adjacent carbons were studied. Results indicate that the reactions observed will depend upon the nature of the two groups. In 2-chlorobutanone, reactions of both functional groups are observed. In allylic compounds the reactions of just one group are seen. In compounds such as 2-chloroethanol one observes the reaction of one group and also a reaction where the two functional groups behave as a "new group" [4].

The second report [10] deals with two functional groups that are removed from each other, i.e., 1,4-bisubstituted butanes. Results indicate that Co^+ would prefer to react at one site over another (halogen $>$ OH), and then eliminate the second functional group, as HX, to give a $\text{Co}(\text{butadiene})^+$ complex [10]. Also it should be noted that the reactions of Co^+ with 1-butanol and 1-chloro- and 1-bromobutanes are more complicated than the propyl and ethyl alcohols and halides discussed earlier. After insertion of the Co^+ ion into the C-Cl or C-Br bond a charge transfer occurs just as in 2-chloropropane, but elimination or retention of HCl or HBr is not observed. What is observed is the loss of H_2 and HCl or HBr yielding $\text{Co}^+(\text{butadiene})$. In 1-butanol, the formation of

$\text{Co}^+(\text{H}_2\text{O})\text{H}_2$ (butadiene) occurs with the subsequent loss of H_2 or H_2 and H_2O .

The last report deals with the chemistry of ions derived from electron impact on $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ with cyclic and linear polyethers [11]. With acyclic polyethers both bare metal ions, Fe^+ and Cr^+ , react by insertion into a C-O bond, followed by a β -H atom shift, and a ligand elimination process. In the cyclic polyether (12-crown-4) multiple metal-ligand interactions are observed. From the initial complex, insertion of the metal into two C-O bonds has been suggested, followed by two β -H atom shifts to give the observed products [11].

When mass spectrometry (MS) is used for chemical analysis, molecular weight, functional group and structural information can frequently be obtained. Of these, molecular weight information, as observed by the formation of the molecular ion, M^+ , is the most useful. Not only is the molecular weight obtained from the parent ion, but, if the M^+ ion is of significant abundance the elemental composition can be determined by isotopic abundance. Unfortunately, many compounds do not give the molecular ion under electron impact (EI) [12].

In 1966, Munson and Field [13] demonstrated the analytical applications of Chemical Ionization (CI) by using CH_4 as a reagent gas and generated spectra in which the analyte molecules reacted with CH_5^+ and C_2H_5^+ (the reagent ions) in the gas phase to form the protonated

molecular ion, $(M+H)^+$, in fairly high abundance. Chemical ionization is considered a "soft" ionization method since less fragmentation is induced as compared to EI.

Unfortunately, due to the small amount of fragmentation that may occur in CIMS, relatively little functional group and structural information is produced.

As discussed earlier, metal centers appear to react in very specific ways with various functional groups. Because of this specific chemistry, metal ions may be used as CI reagents. Freiser, Byrd and Burnier [3] were the first to consider metal ions as CI reagents.

In an effort to evaluate the utility of Metal Ion Chemical Ionization (MICI), generation of some simple rules for spectral interpretation would be much more desirable than the need for generating a Co^+ -CI mass spectral library for compound identification. In an attempt to generate rules of reactivity for multi-functional compounds, we are attempting to answer three basic questions: 1) When will Co^+ react with bifunctional molecules to give results typical of each functional group? 2) When will only one group dominate? 3) When will the two groups behave as a "new group"? The work to date suggests that the answers to these questions will depend not only upon the nature of the two functional groups but also upon their positions relative to each other. The second aspect of this dissertation will deal with the chemistry of various bifunctional organic

molecules with Co^+ . From the results of these experiments, various guidelines for bifunctional compounds were determined.

In most of the studies to date, the reactions of the bare metal ion with the various functional groups were discussed in detail, with very little reported on the chemistry of the other ions formed from electron impact on metal carbonyls, in this case $\text{Co}(\text{CO})_3\text{NO}$. To be specific, the answers to the following questions were sought in the chemistry of various CoL_n^+ ions with monofunctional and bifunctional organic molecules- is the chemistry of these ions identical to Co^+ ? is ligand substitution the only (or dominant) process? Or, do the new reactions based upon $\text{Co}(\text{ligand})^+$ insertion into a bond rather than Co^+ insertion into that bond occur? In this dissertation, the discussion of the chemistry of Co^+ with each compound is followed by a shorter discussion on the chemistry of the various CoL_n^+ ions with that compound.

1

CHAPTER 2

EXPERIMENTAL

A. Principles of Ion Cyclotron Resonance

Ion cyclotron resonance spectrometry is a technique for studying gas phase ion/molecule reactions. Several articles and books have been published on ICR and Fourier Transform Mass Spectrometry (FTMS) theories and principles of operation since 1966 [14-28]. What follows in this chapter is a brief discussion of the principles behind the ion cyclotron resonance experiments. In this technique, ions are produced by electron impact as in other mass spectrometric methods but their subsequent path and means of detection differ greatly from those in a conventional mass spectrometer.

For an ion of mass m , acceleration a , charge e , and a velocity in which v is the velocity vector component perpendicular to the magnetic field B , the force exerted on the ion is given by the equation:

$$F = ma = evB = \frac{mv^2}{r} \quad (1)$$

and this force will be perpendicular to both the magnetic field and velocity. Rearranging Equation (1), one can obtain Equation (2) which describes the motion of the ion in the magnetic field.

$$\frac{mv}{r} = eB \quad (2)$$

As a result the ion's net motion is a circular path (Figure 1) where r is the radius of the orbit.

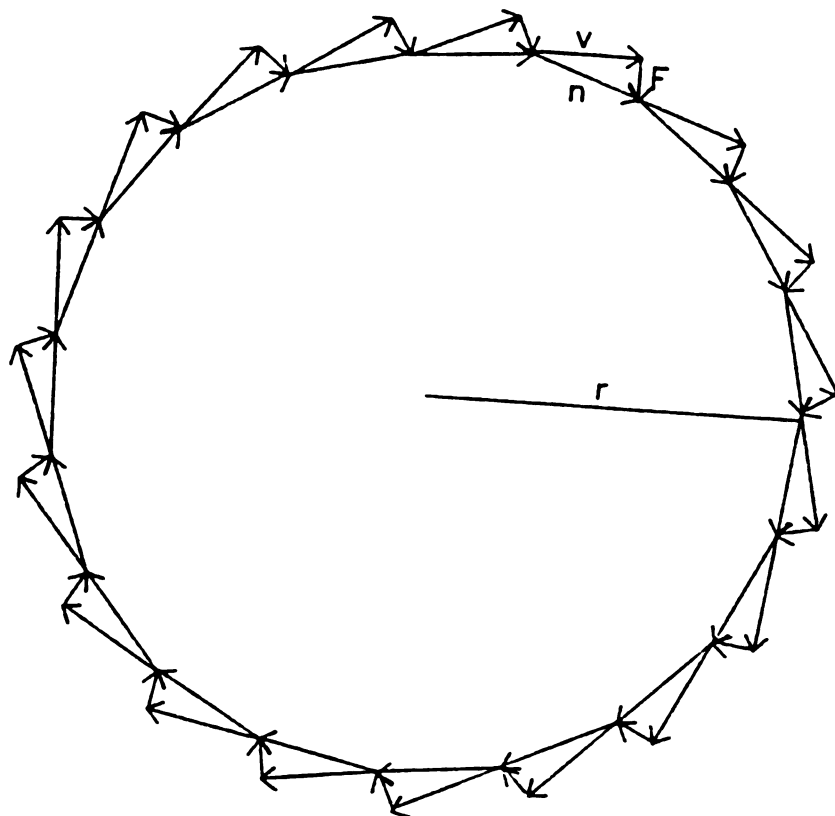


Figure 1. Motion of an ion in a magnetic field.

If velocity has units of cm/sec, and r is in centimeters, one arrives at

$$m\omega_c = eB \quad (3)$$

where ω_c is the angular cyclotron frequency. Rearrangement of Equation (3) gives

$$\omega_c = \frac{eB}{m} \left(\frac{\text{rad}}{\text{sec}} \right)$$
$$\nu_c = \frac{eB}{2\pi m} \left(\frac{\text{cycles}}{\text{sec}} \right)$$

At a constant magnetic field and unit charge, it can be seen from the above equations that heavier ions have a lower cyclotron frequency. It is also important to note that the cyclotron frequency, ω_c or ν_c , is independent of the velocity of the ions.

For detection of a signal in the ICR spectrometer an amplitude limited marginal oscillator is used. The oscillator may be considered a constant current generator which drives a parallel LC circuit at a frequency $\omega_{m.o.}$ (Figure 2). The ICR cell (Figure 3) forms part of the capacitance of this circuit.

When the cyclotron frequency equals the marginal oscillator frequency ($\omega_c = \omega_{m.o.}$) the ions absorb power from the LC circuitry. The output of the marginal oscillator reflects the voltage in the circuit. Since the oscillator

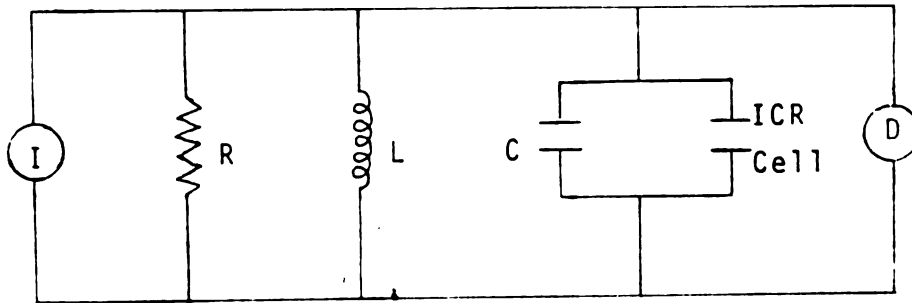


Figure 2. LC tank circuit of marginal oscillator.

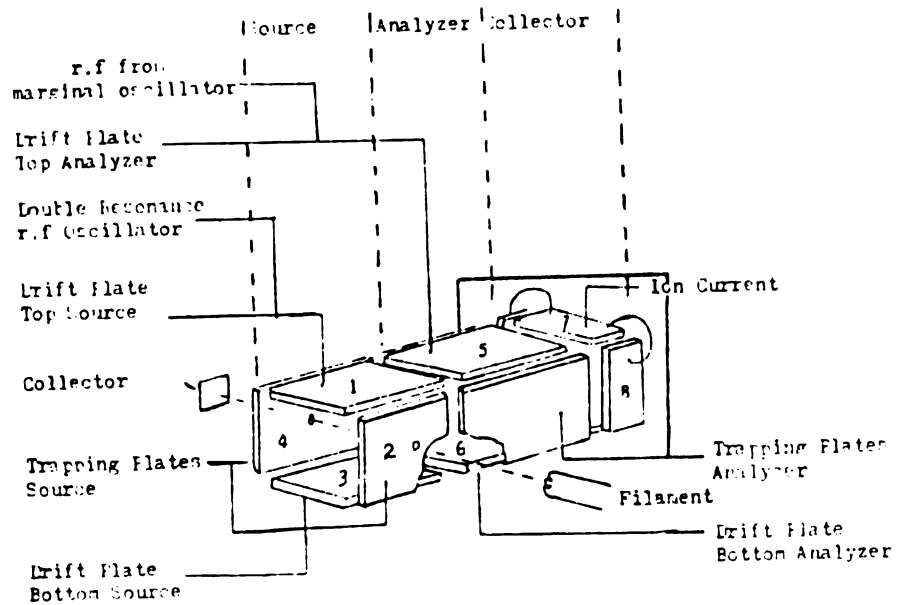


Figure 3. ICR cell.

is driven by a constant current, any change in power ($I \cdot V$) reflects a change voltage in the circuit. The change in voltage (ΔV) is related to the signal intensity. As an ion absorbs power, the ion gains speed and energy. Therefore to maintain its cyclotron frequency, the ion increases its radius in proportion to its gain in velocity. For example if an ion has a cyclotron frequency of 10 orbits/sec and suddenly goes twice as fast, it must increase its orbital radius, its orbital frequency or both. Since the orbital frequency is dependent on mass only, and not energy (Equation (3)), the radius alone will increase.

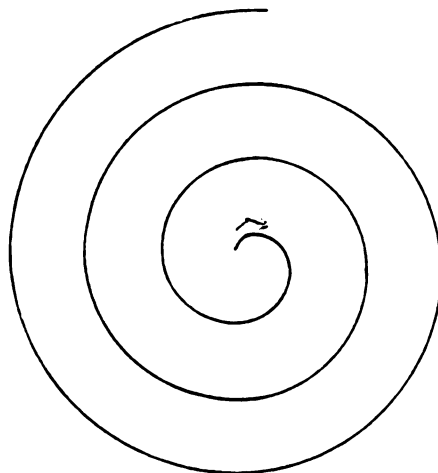


Figure 4. Motion of ion as it absorbs energy.

One method of conducting an ICR experiment is by keeping the marginal oscillator at a constant frequency and varying the cyclotron frequency of the ions by scanning the magnetic field. For convenience, the normal marginal oscillator frequency used is 153.57 KHz; this

will cause a change of one mass unit per change in magnetic field of 100 gauss (.01 tesla) (assuming unit charge).

$$\begin{aligned} v_c &= \frac{1.6021 \times 10^{-19} \text{ C} \times 0.01 \text{ T}}{6.2832 \times 1 \mu \times 1.6604 \times 10^{-23} \text{ kg/w}} \\ &= 1.5359 \times 10^5 + 2 \\ &= 153.57 \text{ kHz} \end{aligned} \tag{4}$$

Other marginal oscillator frequencies are used to increase the mass range (lower M.O. frequency). Decreasing the frequency has the disadvantage of decreasing the resolution and signal intensity.

Equations (1) and (2) describe the force exerted upon nonresonant ions; for resonant ions several other equations describe the force exerted and the power absorption. The force exerted is given by Equation (5):

$$F = \frac{\epsilon_{rf} e}{2} \tag{5}$$

where ϵ_{rf} is the amplitude of the marginal oscillator and the acceleration is

$$a = \frac{\epsilon_{rf} e}{2m}$$

and the additional velocity of the ion in the oscillator field at a frequency $\omega_{M.O.}$ is defined by

$$v = \int_0^t a \, dt = \int_0^t \frac{\epsilon_{rf} e \, dt}{2m} = \frac{\epsilon_{rf} e t}{2m}$$

The instantaneous power absorbed A is the product of the force on the ion and the ion's velocity:

$$A(t) = Fv = \frac{\epsilon_{rf}^2 e^2 t}{4m}$$

The average power drawn by the ion from the rf field while in the detector for a time ($0 < t < \tau$) is

$$A(\tau) = \overline{A(t)} = \frac{1}{\tau} \int_0^t A(t) \, dt = \frac{\epsilon_{rf}^2 e^2 \tau}{8m}$$

The power absorbed by an ion depends inversely on its mass. This mass dependency is due to the way F enters into the acceleration (Equations (1), (5) and (6)).

B. Signal Intensities

The marginal oscillator detector depends upon the power drawn by the ions from a LC circuit in which the upper and lower plates of the analyzer region form a capacitor. Therefore, the signal intensity I_i is

$$I_i = \int A_i(t) P_i(t') \, dt$$

where $P_i(t')$ is the current of all ions of type i , and $A_i(t)$ is the power drawn from the current per ion.

Different time dependences are involved in this equation.

$A_i(t)$ has $t=0$ at the entrance to the analyzer while

$P_i(t')$ has $t=0$ at the electron beam.

For nonreactive ions I_i becomes

$$I_i = \frac{P_i \epsilon_{rf}^2 e^2 \tau^2}{8m_i}$$

The ion current P_i is the equal to

$$P_i = \frac{8m_i I_i}{\epsilon_{rf}^2 e^2 \tau^2}$$

It appears that $P_i \propto m_i I_i$ but that is not strictly true.

Because a spectrum is obtained by sweeping the magnetic field, the dependency of τ on B must be accounted for.

$$\tau \propto \frac{1}{v_{drift}} \propto m \propto B$$

Therefore

$$P_i \propto \frac{I_i m_i}{m_i^2} \propto \frac{I_i}{m_i}$$

To obtain a parameter which is proportional to the relative ionic abundance the signal intensity must be divided by the mass of the ion.

C. Ion Cyclotron Double Resonance

A feature of ICR is the ability to identify precursors of ion/molecule reaction products. This is done by adding

energy to possible reactant ions while monitoring the product ion intensity. When an ion is in resonance at a selected value of B , $m\nu_c$ is constant. Ions of different mass m' can also be brought into resonance at that value of B by supplying a frequency ν'_c such that $m\nu_c = m'\nu'_c$. If m' reacts to give m , exciting m' will cause a change in the amount of m , and this results in a change in the marginal oscillator detector response.

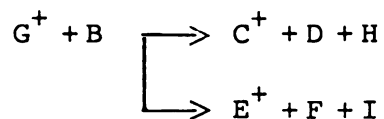
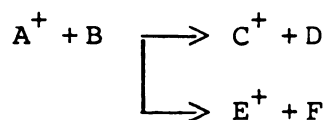
Double resonance experiments are done either with a high power of the double resonance oscillator (ion ejection) or at low power. At a power less than required for ion ejection the following can be implied [28]:

1. A positive ΔI implies either ΔH_{RXN} is positive, or that the reaction has an activation energy that is overcome by heating the ion.
2. A negative ΔI implies that ΔH_{RXN} is negative.
3. A positive ΔH_{RXN} implies that ΔI is positive.
4. A negative ΔH_{RXN} can appear as either a positive or negative ΔI .

A reaction for which ΔI is negative must be occurring without the added energy, and must have a ΔH_{RXN} that is either negative (exothermic reaction) or zero (thermoneutral reaction). A reaction for ΔI is positive means that the rate $k(KE)$ increases as the kinetic energy

of the ion increases. There are a number of reasons why this is the case, being an endothermic reaction (ΔH_{RXN} is positive) is just one reason.

Although low power double resonance can identify the precursors to ion/molecule reactions [23], it cannot be used in determining the product distribution (branching ratios) for a reactant ion. Consider the reactions



in which the two ionic products are produced competitively from the reaction of A^+ and G^+ with B. Only by ejection of A^+ can the contribution of A^+ to C^+ and E^+ be determined.

D. Experimental Set-Up

All experiments were performed using an ion cyclotron resonance (ICR) spectrometer of conventional design that was built at Michigan State University. The three section cell is 0.88 in. \times 0.88 in. \times 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

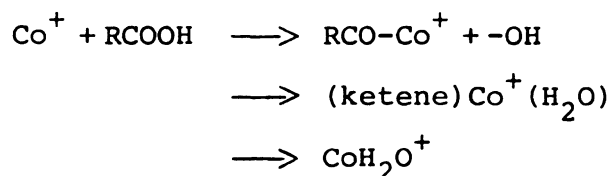
in the source by electron impact with 70 eV electrons. The electron filament is emission regulated. The filament controller and plate voltage controller for the ICR cell were designed and constructed at MSU. The instrument is operable in the pulsed or drift ICR modes. Data in this dissertation were obtained under normal drift mode conditions by using trapping voltage modulation and phase sensitive detection. The marginal oscillator detector is based upon the design of Warnick, Anders and Sharp [29]. Ion cyclotron double resonance experiments were performed to identify precursor of ion/molecule reaction products with the use of a Wavetek Model 144 sweep generator as the secondary oscillator. 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 a 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.

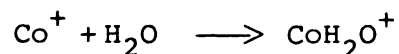
Tricarbonylnitrosylcobalt(0) and 2-bromoethanol were obtained from Alfa Products. All allylic compounds

2-chloroethanol, butanone, propanoic, butanoic, 2-butenic and 2-chloropropionic acids were obtained from Chem Services, Inc. 3-Butenone was obtained from Columbia Organic Chemical Company. 3-Chlorobutanone, 2,2-dimethylpropanoic and 2-bromoacetic acids were purchased from Aldrich Chemical Company. 3-Chloropropanoic acid was obtained from Crescent Chemical Company. Acetic acid was purchase from J.T. Baker Chemical Company. 3-Hydroxypropanoic acid was purchased from Pfaltz and Bauer. Deuterated acetic (d_4) and propanoic (d_6) acids were obtained from MSD Isotopes. All other compounds were obtained from Fluka Chemical Corporation.

In the reactions of the cobalt-containing ions with the unsubstituted carboxylic acids one product observed was CoH_2O^+ formed by the following reaction:



If the acid was not pure but contained any water the above reaction could not be distinguished from



In order to verify the purity of the unsubstituted acids, low pressure electron impact spectra were obtained on

the ICR and examined for any peaks corresponding to fragments of H_2O . None were observed for the unsubstituted acids except for 2,2-dimethylpropanoic acid. This acid was then dried and purified by vacuum sublimation.

The low pressure EI mass spectra of the substituted carboxylic acids showed in most cases the presence of water. The first attempt at purifying the solid carboxylic acids was recrystallization from anhydrous ether. Samples were recrystallized at least three times from ether. When admitted to the ICR, the mass spectrum of ethyl ether was obtained. The solvent could not be removed from the sample under vacuum, so a dry technique of purification was used. 3-Bromopropanoic, 2-bromoacetic, 3-chloropropanoic, 2-chloroacetic and 2-hydroxyacetic acids were purified by sublimation.

The liquid acids, 2-mercaptoacetic, 2-mercapto-propanoic and 3-hydroxypropanoic acids also contained small amounts of water. Several different approaches were used in attempts to purify these compounds. First, pumping on the sample under vacuum (<100 mtorr) was employed in the hope that the higher vapor pressure components would be lost. This did not work. Next, distillation of 2-mercaptoacetic acid at atmospheric pressure did not accomplish any positive results. Vacuum distillations were attempted and these also were futile.

More drastic means were then attempted for the purification of the mercapto-acids, P_2O_5 and molecular

sieves did not remove the water. Several attempts at continuous extractions were done by refluxing the acids in benzene and azetroping off the water with the benzene by using a Dean-Stark trap. After refluxing for at least three hours, the samples were then rotary evaporated or vacuum distilled to remove benzene. Both methods left traces of benzene in the sample. Similar reflux was also done using ether as the solvent.

Since the mercapto acids seemed to prefer to retain the solvents used in the extraction, a final attempt at vacuum distillation was tried. The vacuumed distilled acids were analyzed by gas chromatography using a thermocouple detector and were found not to contain water. As a second check, a EI spectrum was obtained on the department's Finnigan GC/MS, again no traces of water. When these compounds were analyzed on the ICR no traces of water were detected.

2-Hydroxypropanoic acid caused a new problem in an attempt to purify it. This acid readily reacts with a second mole of this acid to give off two moles of H_2O when heated (even under vacuum). The methods used in purifying the mercapto acids were attempted here but were useless. To purify this acid, the sample was placed in a vacuum dessicator in which P_2O_5 was used. It was left undisturbed for 48 hours and then analyzed on the ICR. The EI spectrum indicated that the water was removed.

These purified samples and all other compounds were subjected to multiple freeze-pump-thaw cycles before use.

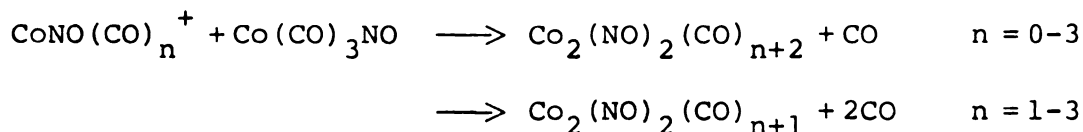
In a typical experiment, low pressure electron impact (EI) spectra of the organic compound to be studied were recorded to determine purity. Higher pressure spectra were obtained and any ion/molecule reactions due to the organic system alone were identified and their precursors determined by ion cyclotron double resonance. Then spectra were obtained of 1:1 and 1:2 mixtures of $\text{Co(CO)}_3\text{NO}$: organic for total pressures up to 1.5×10^{-5} torr (as measured by an ionization gauge). Ion/molecule reaction products were identified and precursors of each determined by double resonance techniques. The observed reactions are facile and have a rate constant within an order of magnitude of the collision frequency. A branching ratio is the percentage of an observed reaction is of the total for a given ion. In the Introduction a branching ratio of 60% was given for the formation of CoC_3H_6^+ from 2-chloropropane. In other words, 60% of all the products of 2-chloropropane with Co^+ is CoC_3H_6^+ . Branching ratios are accurate to within 10%.

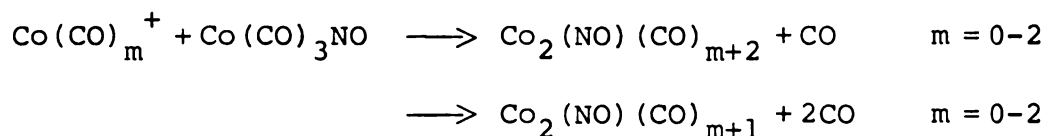
CHAPTER 3

THE CHEMISTRY OF COBALT-CONTAINING IONS WITH THIOLS

Before discussing the chemistry of the cobalt and cobalt-containing ions with the different organic compounds, a brief discussion of the mass spectrum of $\text{Co}(\text{CO})_3\text{NO}$ is necessary. At 70 ev, the parent ion, $\text{Co}(\text{CO})_3\text{NO}^+$ ($m/z = 173$), is abundant. Ions are also observed due to the loss of one, two or three carbonyls ($\text{Co}(\text{CO})_2\text{NO}^+$ ($m/z = 145$), CoCONO^+ ($m/z = 117$) and CoNO^+ ($m/z = 89$)) with the abundance decreasing with the loss of more CO's. Ions are also observed that do not contain a NO ligand ($\text{Co}(\text{CO})_2^+$ ($m/z = 115$), CoCO^+ ($m/z = 87$) and Co^+ ($m/z = 59$)). The bare metal ion is the most abundant ion in the 70 ev mass spectrum.

At higher pressures of $\text{Co}(\text{CO})_3\text{NO}$, reactions of these ions with the neutral $\text{Co}(\text{CO})_3\text{NO}$ are observed [30].

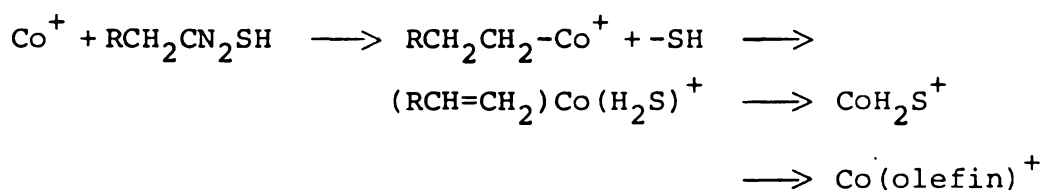




In this study the reactions of these binuclear metal ions were not investigated.

A. The Chemistry of Co^+ with Thiols

The primary site of attack by Co^+ in thiols is apparently the polar C-SH bond. Reactions following Co^+ insertion at this site account for a minimum of 90% of the products observed for all of the thiols studied except for 2-methyl-1-propanethiol. For all of the thiols, except 1-butanethiol and 2-butanethiol, the only products observed following a reaction sequence similar to Scheme I are CoH_2S^+ and $\text{Co}(\text{olefin})^+$



where retention of the olefin is the slightly favored pathway. This preference of Co^+ for the olefin follows metal-ligand "affinities". Several reports in the past few years have pointed out the correlation between proton affinities and metal-ligand affinities [10,30-38]. In general, when two or more ligands compete for sites on a

metal, the ligand that has the lower proton affinity is apparently the "poorer ligand" (lower bond strength to the metal ion) and is eliminated to a greater extent than the other ligands. (Relevant proton affinities are given in Appendix A.)

1. Ethanethiol

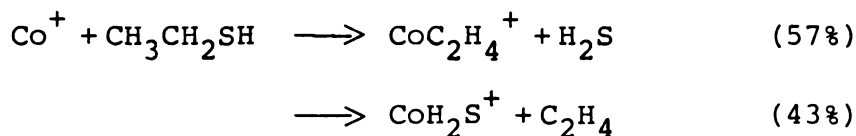
In Table 1 are the reactions of each metal ion in the mixture $\text{Co}(\text{CO})_3\text{NO}$ and ethanethiol along with the branching ratios.

In the chemistry of Co^+ with ethanol an exception to the above proton affinity/metal-ligand affinity trend occurs when H_2O and $\text{CH}_2=\text{CH}_2$ compete as ligands in the $(\text{C}_2\text{H}_4)\text{Co}^+(\text{H}_2\text{O})$ complex. In this case the metal prefers to retain the olefin which has a lower proton affinity than water.

When Co^+ reacts with ethanethiol, retention of the ethene is preferred rather than H_2S , although the latter has the higher proton affinity. In the Co^+ /ethanol system, retention of water constituted 13% of the reactions while in the Co^+ /ethanethiol system retention of H_2S accounted for 43% of the products. This difference may be due to the higher proton affinity of the H_2S which competes more effectively with the olefin than does water for a site on the metal. (Note, the percentages after each reaction are the branching ratios.)

Table 1. Reactions of the ions derived from $\text{Co}(\text{CO})_3\text{NO}$ with ethanethiol ($\text{M} = \text{CH}_3\text{CH}_2\text{SH}$).

Co^+	$+ \text{M} \longrightarrow$	$\text{CoC}_2\text{H}_4^+ + \text{H}_2\text{S}$	(57%)
	\longrightarrow	$\text{CoH}_2\text{S}^+ + \text{C}_2\text{H}_4$	(43%)
CoCO^+	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2^+$	$+ \text{M} \longrightarrow$	$\text{CoCOM}^+ + \text{CO}$	(100%)
CoNO^+	$+ \text{M} \longrightarrow$	No Reaction	
CoCONO^+	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(60%)
	\longrightarrow	$\text{CoCONOM}^+ + \text{CO}$	(40%)
$\text{Co}(\text{CO})_3\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoCONOM}^+ + 2\text{CO}$	(100%)

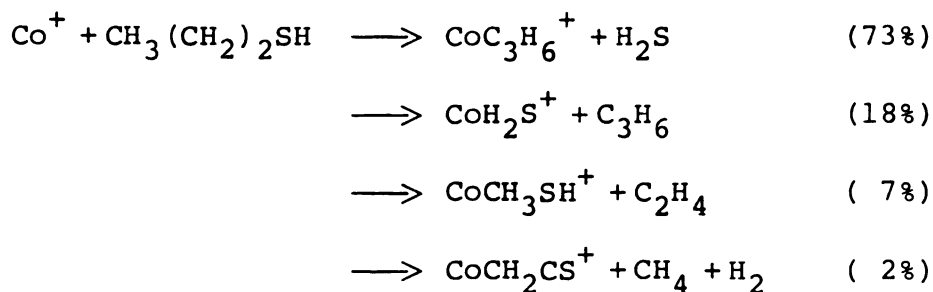


The chemistry of Co^+ with ethanethiol has been previously reported [6]. The product CoSH^+ , however, was not observed in our experiments. Also the branching ratios are different from those we obtained but the ordering of the reactions is the same, that is, retention of C_2H_4 by Co^+ was favored over H_2S retention.

2. Propanethiols

In Tables 2 and 3 are the reactions of each metal ion with 1-propanethiol and 2-propanethiol, respectively, along with the branching ratios.

Besides the formation of $\text{Co}(\text{olefin})^+$ and CoH_2S^+ , two other reactions are observed with 1-propanethiol.



The third reaction in this mixture involves Co^+ insertion into the $\text{C}_1\text{-C}_2$ bond, followed by a $\beta\text{-H}$ atom shift to form the $\text{Co}(\text{C}_2\text{H}_4)(\text{CH}_3\text{SH})^+$ complex from which elimination of ethene occurs. In this reaction, retention of CH_3SH is

Table 2. Reactions of the ions derived from $\text{Co}(\text{CO})_3\text{NO}$ with 1-propanethiol ($\text{M} = \text{CH}_3(\text{CH}_2)_2\text{SH}$).

Co^+	$+ \text{M} \longrightarrow$	$\text{CoC}_3\text{H}_6^+ + \text{H}_2\text{S}$	(73%)
	\longrightarrow	$\text{CoH}_2\text{S}^+ + \text{C}_3\text{H}_6$	(18%)
	\longrightarrow	$\text{CoCH}_3\text{SH}^+ + \text{C}_2\text{H}_4$	(7%)
	\longrightarrow	$\text{CoCH}_2=\text{C}=\text{S}^+ + \text{CH}_4 + \text{H}_2$	(2%)
CoCO^+	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(10%)
	\longrightarrow	$\text{CoCOC}_3\text{H}_6^+ + \text{H}_2\text{S}$	(3%)
	\longrightarrow	$\text{CoC}_3\text{H}_6^+ + \text{H}_2\text{S} + \text{CO}$	(75%)
	\longrightarrow	$\text{CoCOCH}_3\text{SH}^+ + \text{C}_2\text{H}_4$	(5%)
	\longrightarrow	$\text{CoCH}_2=\text{C}=\text{S}^+ + \text{CH}_4 + \text{H}_2 + \text{CO}$	(7%)
$\text{Co}(\text{CO})_2^+$	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + 2\text{CO}$	(30%)
	\longrightarrow	$\text{CoCOM}^+ + \text{CO}$	(70%)
CoNO^+	$+ \text{M} \longrightarrow$	$\text{CoNOH}_2\text{S}^+ + \text{C}_3\text{H}_6$	(66%)
	\longrightarrow	$\text{CoNOC}_3\text{H}_6^+ + \text{H}_2\text{S}$	(34%)
CoCONO^+	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(25%)
	\longrightarrow	$\text{CoCONOC}_3\text{H}_6^+ + \text{H}_2\text{S}$	(4%)
	\longrightarrow	$\text{CoNOC}_3\text{H}_6^+ + \text{H}_2\text{S} + \text{CO}$	(5%)
	\longrightarrow	$\text{CoNOCH}_2=\text{C}=\text{S}^+ + \text{CH}_4 + \text{H}_2 + \text{CO}$	(66%)

Table 2 Continues.

Table 2 Continued.

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$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 2\text{CO}$	(78%)
	$\longrightarrow \text{CoCONOM}^+ + \text{CO}$	(5%)
	$\longrightarrow \text{Co}(\text{CO})_2\text{NOCH}_2\text{SH}^+ + \text{C}_2\text{H}_5$	(17%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoCONOM}^+ + 2\text{CO}$	(100%)
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Table 3. Reactions of the ions derived from $\text{Co}(\text{CO})_3\text{NO}$ with 2-propanethiol ($\text{M} = (\text{CH}_3)_2\text{CHSH}$).

$\text{CO}^+ + \text{M} \longrightarrow$	$\text{CoC}_3\text{H}_6^+ + \text{H}_2\text{S}$	(59%)
	$\longrightarrow \text{CoH}_2\text{S}^+ + \text{C}_3\text{H}_6$	(41%)
$\text{CoCO}^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(1%)
	$\longrightarrow \text{CoC}_3\text{H}_6^+ + \text{H}_2\text{S} + \text{CO}$	(72%)
	$\longrightarrow \text{CoCOC}_3\text{H}_6^+ + \text{H}_2\text{S}$	(8%)
	$\longrightarrow \text{CoCOH}_2\text{S}^+ + \text{C}_3\text{H}_6$	(12%)
	$\longrightarrow \text{CoCH}_2=\text{C}=\text{S}^+ + \text{CH}_3\text{CHO} + \text{H}_2$	(7%)
$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow$	$\text{CoCOM}^+ + \text{CO}$	(60%)
	$\longrightarrow \text{CoM}^+ + 2\text{CO}$	(10%)
	$\longrightarrow \text{CoCOC}_3\text{H}_6^+ + \text{H}_2\text{S} + \text{CO}$	(30%)
$\text{CoNO}^+ + \text{M} \longrightarrow$	$\text{CoNOH}_2\text{S}^+ + \text{C}_3\text{H}_6$	(77%)
	$\longrightarrow \text{CoNOC}_3\text{H}_6^+ + \text{H}_2\text{S}$	(23%)
$\text{CoCONO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(34%)
	$\longrightarrow \text{CoCONOC}_3\text{H}_6^+ + \text{H}_2\text{S}$	(10%)
	$\longrightarrow \text{CoNOC}_3\text{H}_6^+ + \text{H}_2\text{S} + \text{CO}$	(10%)
	$\longrightarrow \text{CoNOCH}_2=\text{C}=\text{S}^+ + \text{CH}_3\text{CHO} + \text{H}_2$	(46%)

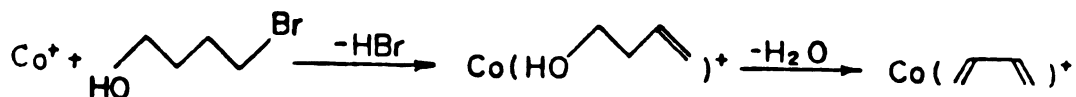
Table 3 Continues.

Table 3 Continued.

$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 2\text{CO}$	(75%)
	$\longrightarrow \text{CoCONOM}^+ + \text{CO}$	(10%)
	$\longrightarrow \text{Co}(\text{CO})_2\text{NOCH}_2\text{SH}^+ + \text{C}_2\text{H}_5$	(15%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoCONOM}^+ + 2\text{CO}$	(100%)

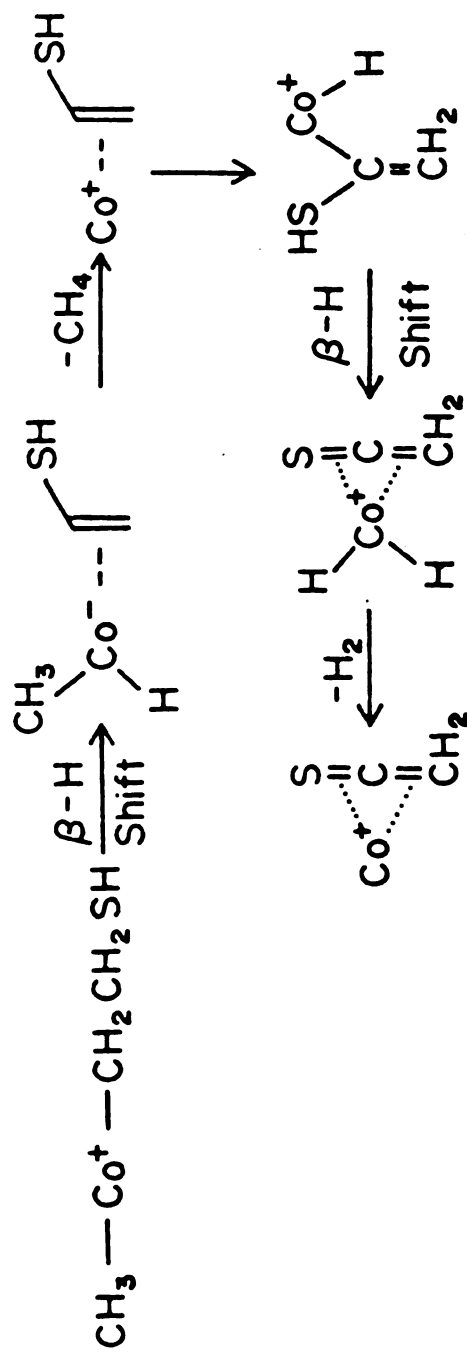
preferred over $\text{CH}_2=\text{CH}_2$, consistent with the greater proton affinity of metanethiol (therefore the greater metal-ligand affinity).

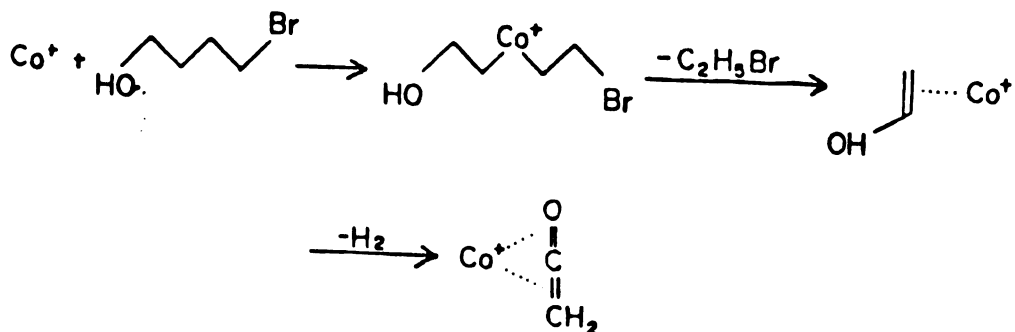
The fourth reaction, leading to the formation of Co^+ -thioketene, presumably involves the insertion of Co^+ into the C_2-C_3 bond, leading to either the intermediate $(\text{CH}_4)\text{Co}(\text{C}_2\text{H}_3\text{SH})^+$, or $\text{Co}(\text{C}_2\text{H}_3\text{SH})^+$, in which $\text{C}_2\text{H}_3\text{SH}$ rapidly loses H_2 . A mechanism is suggested in Scheme II. Transition metal ion-ketene complexes have previously been observed as reaction products [3,9,39]. The $\text{CoC}_2\text{H}_3\text{SH}^+$ intermediate was not observed. It is interesting to note that in some reactions involving multistep elimination processes, the intermediates are observed. For example, in the reaction of Co^+ with 4-bromo-1-butanol [9]



both $\text{Co}(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH})^+$ and $\text{Co}(\text{CH}_2=\text{CHCH}=\text{CH}_2)^+$ are observed as products. However, a reaction also occurs leading to

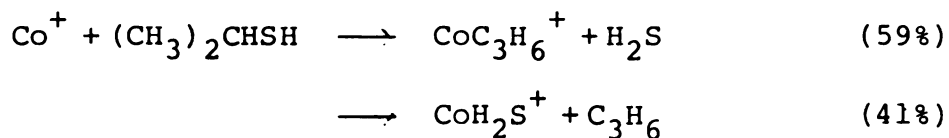
Scheme II





the product $\text{Co}(\text{CH}_2=\text{C}=\text{O})^+$. The $\text{Co}(\text{CH}_2=\text{CHOH})^+$ intermediate is not observed, analogous to what is reported here for the formation of $\text{Co}(\text{CH}_2=\text{C}=\text{S})^+$ from 1-propanethiol.

In 2-propanethiol only the products following Co^+ insertion into the C-SH bond were observed.



Here the metal-ligand bond strengths, as suggested by proton affinities, are consistent with the results. The ligand with the higher proton affinity is retained to a greater extent by the metal.

3. Butanethiols

In Tables 4 through 7 are the reactions of each metal ion with the isomeric butanethiols along with the branching ratios.

Table 4. Reactions of the ions derived from $\text{Co}(\text{CO})_3\text{NO}$ with 1-butanethiol ($\text{M} = \text{CH}_3(\text{CH}_2)_3\text{SH}$).

Co^+	$+ \text{M} \longrightarrow$	$\text{CoC}_4\text{H}_8^+ + \text{H}_2\text{S}$	(17%)
	\longrightarrow	$\text{CoH}_2\text{S}^+ + \text{C}_4\text{H}_8$	(5%)
	\longrightarrow	$\text{CoC}_2\text{H}_4^+ + \text{CH}_3\text{CH}_2\text{SH}$	(5%)
	\longrightarrow	$\text{C}_4\text{H}_9^+ + \text{CoSH}$	(11%)
	\longrightarrow	$\text{CoC}_4\text{H}_6^+ + \text{H}_2 + \text{H}_2\text{S}$	(38%)
	\longrightarrow	$\text{CoC}_4\text{H}_6(\text{H}_2\text{S})^+ + \text{H}_2$	(23%)
CoCO^+	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(14%)
	\longrightarrow	$\text{CoCOC}_4\text{H}_8^+ + \text{H}_2\text{S}$	(13%)
	\longrightarrow	$\text{CoC}_4\text{H}_8^+ + \text{H}_2\text{S} + \text{CO}$	(29%)
	\longrightarrow	$\text{CoCOH}_2\text{S}^+ + \text{C}_4\text{H}_8$	(44%)
$\text{Co}(\text{CO})_2^+$	$+ \text{M} \longrightarrow$	$\text{CoCOM}^+ + \text{CO}$	(76%)
	\longrightarrow	$\text{CoM}^+ + 2\text{CO}$	(16%)
	\longrightarrow	$\text{CoCOC}_4\text{H}_8^+ + \text{H}_2\text{S} + \text{CO}$	(8%)
CoNO^+	$+ \text{M} \longrightarrow$	No Reaction	
CoCONO^+	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(100%)
$\text{Co}(\text{CO})_3\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoCONOM}^+ + 2\text{CO}$	(100%)

Table 5. Reactions of the ions derived from $\text{Co}(\text{CO})_3\text{NO}$ with 2-butanethiol ($\text{M} = \text{CH}_3\text{CH}_2\text{CHSHCH}_3$).

Co^+	$+ \text{M} \longrightarrow$	$\text{CoC}_4\text{H}_8^+ + \text{H}_2\text{S}$	(31%)
	\longrightarrow	$\text{CoH}_2\text{S}^+ + \text{C}_4\text{H}_8$	(6%)
	\longrightarrow	$\text{CoC}_3\text{H}_6^+ + \text{CH}_3\text{SH}$	(5%)
	\longrightarrow	$\text{C}_4\text{H}_9^+ + \text{CoSH}$	(10%)
	\longrightarrow	$\text{CoC}_4\text{H}_6^+ + \text{H}_2 + \text{H}_2\text{S}$	(10%)
	\longrightarrow	$\text{CoC}_4\text{H}_6(\text{H}_2\text{S})^+ + \text{H}_2$	(38%)
CoCO^+	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(10%)
	\longrightarrow	$\text{CoCOC}_4\text{H}_8^+ + \text{H}_2\text{S}$	(45%)
	\longrightarrow	$\text{CoC}_4\text{H}_8^+ + \text{H}_2\text{S} + \text{CO}$	(15%)
	\longrightarrow	$\text{CoCOH}_2\text{S}^+ + \text{C}_4\text{H}_8$	(19%)
	\longrightarrow	$\text{CoC}_3\text{H}_6^+ + \text{CH}_3\text{SH} + \text{CO}$	(11%)
$\text{Co}(\text{CO})_2^+$	$+ \text{M} \longrightarrow$	$\text{CoCOM}^+ + \text{CO}$	(56%)
	\longrightarrow	$\text{CoM}^+ + 2\text{CO}$	(16%)
	\longrightarrow	$\text{CoCOC}_4\text{H}_8^+ + \text{H}_2\text{S} + \text{CO}$	(13%)
	\longrightarrow	$\text{Co}(\text{CO})_2\text{C}_4\text{H}_8^+ + \text{H}_2\text{S}$	(15%)
CoNO^+	$+ \text{M} \longrightarrow$	No Reaction	
CoCONO^+	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(100%)
$\text{Co}(\text{CO})_3\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoCONOM}^+ + 2\text{CO}$	(100%)

Table 6. Reactions of the ions derived from $\text{Co}(\text{CO})_3\text{NO}$ with 2 methyl-1-propanethiol ($\text{M} = (\text{CH}_3)_2\text{CHCH}_2\text{SH}$).

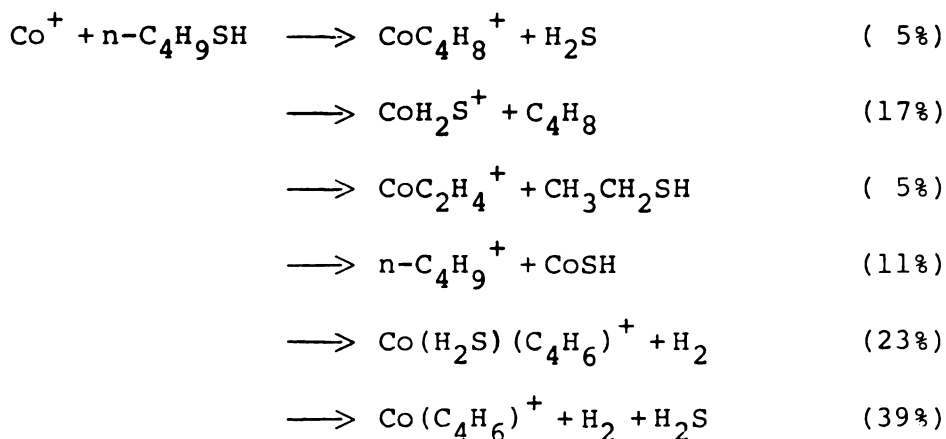
Co^+	$+ \text{M} \longrightarrow$	$\text{CoC}_4\text{H}_8^+ + \text{H}_2\text{S}$	(15%)
	\longrightarrow	$\text{CoH}_2\text{S}^+ + \text{C}_4\text{H}_8$	(60%)
	\longrightarrow	$\text{CoCH}_3\text{SH}^+ + \text{C}_3\text{H}_6$	(24%)
	\longrightarrow	$\text{CoC}_3\text{H}_6^+ + \text{CH}_3\text{SH}$	(1%)
CoCO^+	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(19%)
	\longrightarrow	$\text{CoCOC}_4\text{H}_8^+ + \text{H}_2\text{S}$	(15%)
	\longrightarrow	$\text{CoC}_4\text{H}_8^+ + \text{H}_2\text{S} + \text{CO}$	(62%)
	\longrightarrow	$\text{CoC}_3\text{H}_6^+ + \text{CH}_3\text{SH} + \text{CO}$	(4%)
$\text{Co}(\text{CO})_2^+$	$+ \text{M} \longrightarrow$	$\text{CoCOM}^+ + \text{CO}$	(100%)
CoNO^+	$+ \text{M} \longrightarrow$	No Reaction	
CoCONO^+	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(100%)
$\text{Co}(\text{CO})_3\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoCONOM}^+ + 2\text{CO}$	(100%)

Table 7. Reactions of the ions derived from $\text{Co}(\text{CO})_3\text{NO}$ with 2-methyl-2-propanethiol ($\text{M} = (\text{CH}_3)_3\text{CSH}$).

Co^+	$+ \text{M} \longrightarrow$	$\text{CoC}_4\text{H}_8^+ + \text{H}_2\text{S}$	(59%)
	\longrightarrow	$\text{CoH}_2\text{S}^+ + \text{C}_4\text{H}_8$	(41%)
CoCO^+	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(16%)
	\longrightarrow	$\text{CoCOC}_4\text{H}_8^+ + \text{H}_2\text{S}$	(30%)
	\longrightarrow	$\text{CoC}_4\text{H}_8^+ + \text{H}_2\text{S} + \text{CO}$	(21%)
	\longrightarrow	$\text{CoCOH}_2\text{S}^+ + \text{C}_4\text{H}_8$	(33%)
$\text{Co}(\text{CO})_2^+$	$+ \text{M} \longrightarrow$	$\text{CoCOM}^+ + \text{CO}$	(51%)
	\longrightarrow	$\text{CoCOC}_4\text{H}_8^+ + \text{H}_2\text{S} + \text{CO}$	(49%)
CoNO^+	$+ \text{M} \longrightarrow$	No Reaction	
CoCONO^+	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(32%)
	\longrightarrow	$\text{CoNOC}_4\text{H}_8^+ + \text{H}_2\text{S} + \text{CO}$	(68%)
$\text{Co}(\text{CO})_2\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(89%)
	\longrightarrow	$\text{CoCONOM}^+ + \text{CO}$	(11%)
$\text{Co}(\text{CO})_3\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoCONOM}^+ + 2\text{CO}$	(100%)

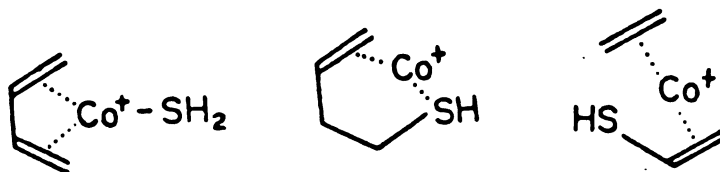
In 1-butanethiol, the C-SH bond is still the primary site of insertion by Co^+ , but several new products are observed. First, Co^+ reacts by hydrogen sulfide anion abstraction to give the butyl cation in this compound. This alkyl cation formation process has been observed in the chemistry of Co^+ with numerous alkyl halides [5,6] and 2-propanol [5]. In nitroalkanes [6], RNO_2 abstraction of NO_2^- increases as the alkyl group increases in size- 0% for $\text{R}=\text{CH}_3$ and $\text{R}=\text{C}_2\text{H}_5$, 12% for $\text{R}=\text{n-C}_3\text{H}_7$, 38% for $\text{R}=\text{n-C}_4\text{H}_9$ and up to 79% for $\text{R}=\text{t-C}_4\text{H}_9$ -since, as the size of the alkyl group increases, its ionization potential decreases, energetically facilitating alkyl cation formation.

In Scheme III, the reactions of 1-butanethiol with Co^+ are shown. For 1-butanethiol, after the initial insertion into the C-SH bond and the β -H atom shift, structure I is obtained. From this intermediate, products observed for all thiols, CoH_2S^+ and $\text{Co}(\text{butene})^+$ are formed.

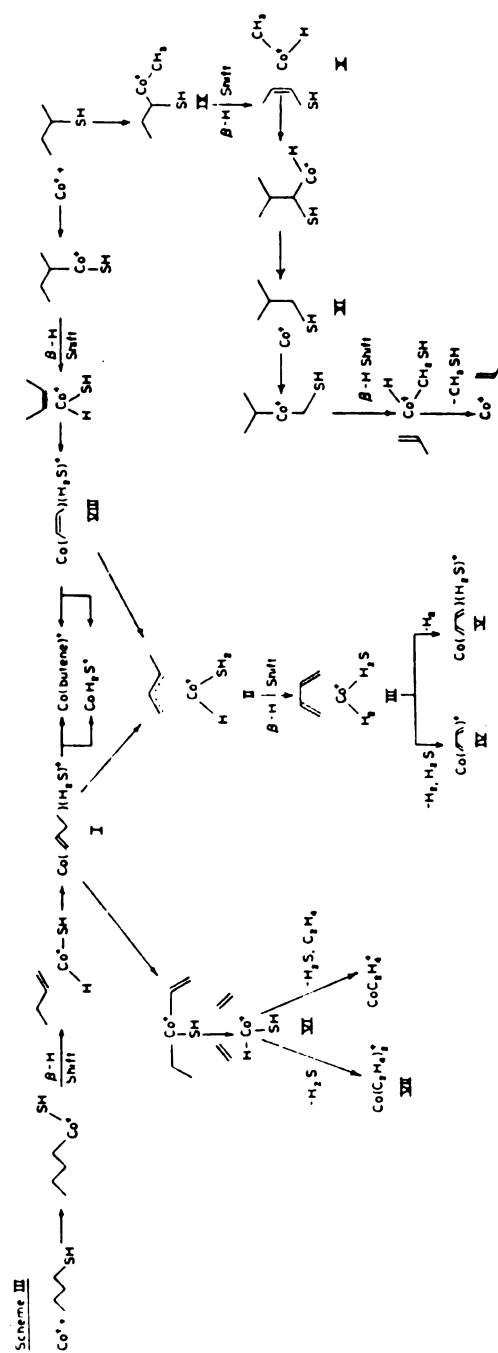


Co^+ can also insert into the allylic C-H bond of structure I to give structure II followed by a β -H shift to the metal to give an intermediate III $\text{Co}(\text{butadiene})(\text{H}_2\text{S})(\text{H}_2)^+$, from which elimination of H_2 or H_2 and H_2S can occur. This insertion process has been previously suggested for the reaction of Co^+ with 1-butene and 2-butene [9].

Structure III is one of the three possible pathways through which 1-butanethiol may eliminate H_2 . Using the approach which Tsarbopoulos and Allison used to explain H_2 elimination from 1-butanol [10], the following three structures as products following H_2 elimination from 1-butanethiols are feasible.

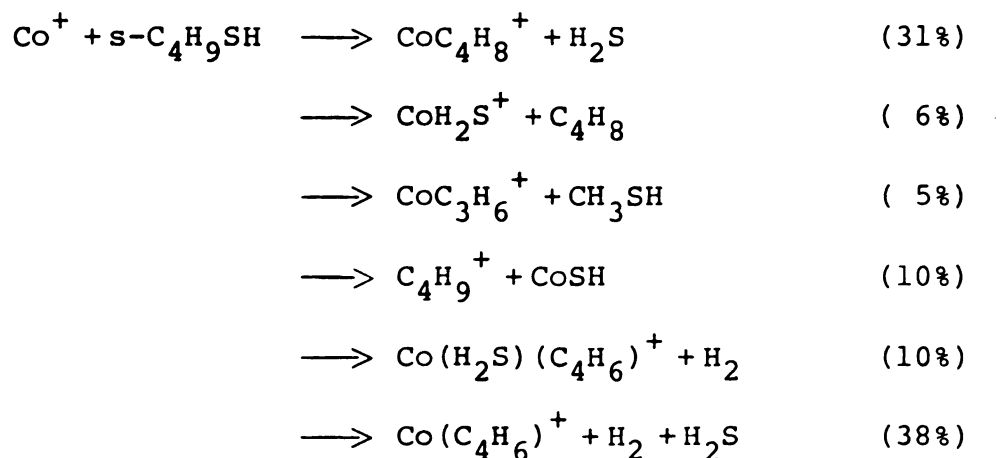


Armentrout and Beauchamp have reported that Co^+ inserts into the $\text{C}_2\text{-C}_3$ bond of 1-butene to eliminate ethene [9]. This could also occur in 1-butanethiol. After the formation of structure I, the Co^+ inserts into the $\text{C}_2\text{-C}_3$ bond of I followed by a β -H shift to the metal and rearrangement into structure VI. From structure VI, H_2S elimination occurs to give $\text{Co}(\text{C}_2\text{H}_4)_2^+$, which has the

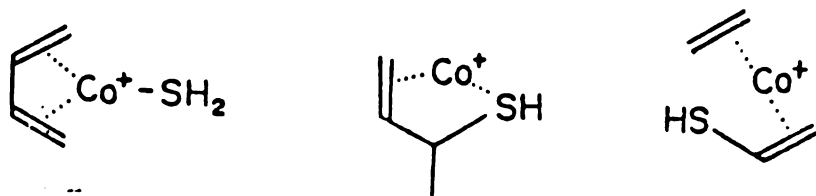


same empirical formula as $\text{Co}(\text{Butene})^+$. Therefore, the first reaction in this mixture has two possible structures for the ionic product. More importantly, the elimination of H_2S and C_2H_4 giving CoC_2H_4^+ cannot be explained through competitive elimination just as it was for ethanethiol.

In the reactions of 2-butanethiol with Co^+ , abstraction of SH^- giving the butyl cation is observed, as well as, the formation of CoH_2S^+ and $\text{Co}(\text{butene})^+$.

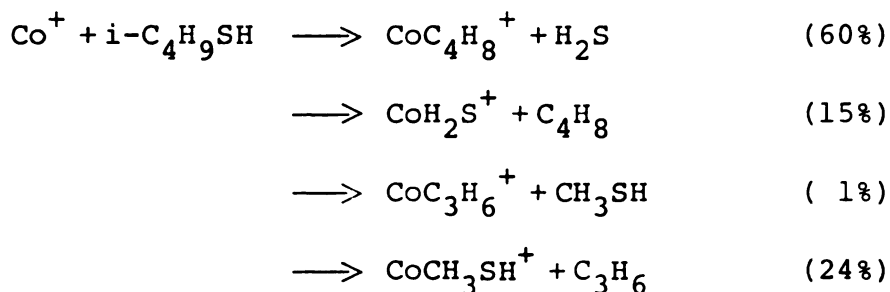


The chemistry of Co^+ with 2-butanethiol is also shown in Scheme III. From structure VIII, $\text{Co}(\text{2-butene})(\text{H}_2\text{S})^+$, insertion into the C-H bond is possible giving structure II from which H_2 or H_2 and H_2S elimination may occur as in 1-butanethiol. As in explaining H_2 elimination from 1-butanethiol, several structures are possible for H_2 elimination from 2-butanethiol.



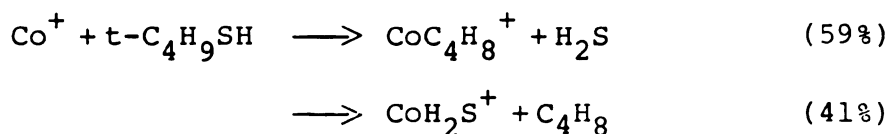
The elimination of methanethiol from 2-butanethiol could be explained through isomerization of 2-butanethiol to 2-methyl-1-propanethiol (isobutyl thiol). Co^+ inserts into the $\text{C}_1\text{-C}_2$ bond of 2-butanethiol to give structure IX, which is then followed by a $\beta\text{-H}$ atom shift to the metal (structure X), then rearrangement to $\text{Co}^+(\text{iso-butyl thiol})$, structure XI. From this intermediate Co^+ then inserts into the $\text{C}_1\text{-C}_2$ bond and a $\beta\text{-H}$ atom shift to give $\text{Co}(\text{C}_3\text{H}_6)(\text{CH}_3\text{SH})^+$. The proton affinities of the two ligands are close to each other, and as in the case of ethanethiol when the proton affinities are close enough it appears that the olefin is preferred even though it has the lower proton affinity. This may be due to a stronger interaction of Co^+ with the π -electrons in the olefin than with the lone pair on the hetero atom. Isomerization of 2-substituted butyl compounds has been suggested in the chemistry of Co^+ with amines [7] and of TiCl_3^+ with 2-butanone [40].

In the chemistry of Co^+ with 2-methyl-1-propanethiol 75% of the reactions are derived from the $\text{Co}(\text{butene})(\text{H}_2\text{S})^+$ intermediate.



The remaining 25% of the products are due to Co^+ insertion into C-C bond of 2-methyl-1-propanethiol.

In 2-methyl-2-propanethiol, insertion into the C-SH bond followed by the β -H shift and then competitive ligand loss is the only process observed. The two products observed reflect the metal ligand affinities as expected.



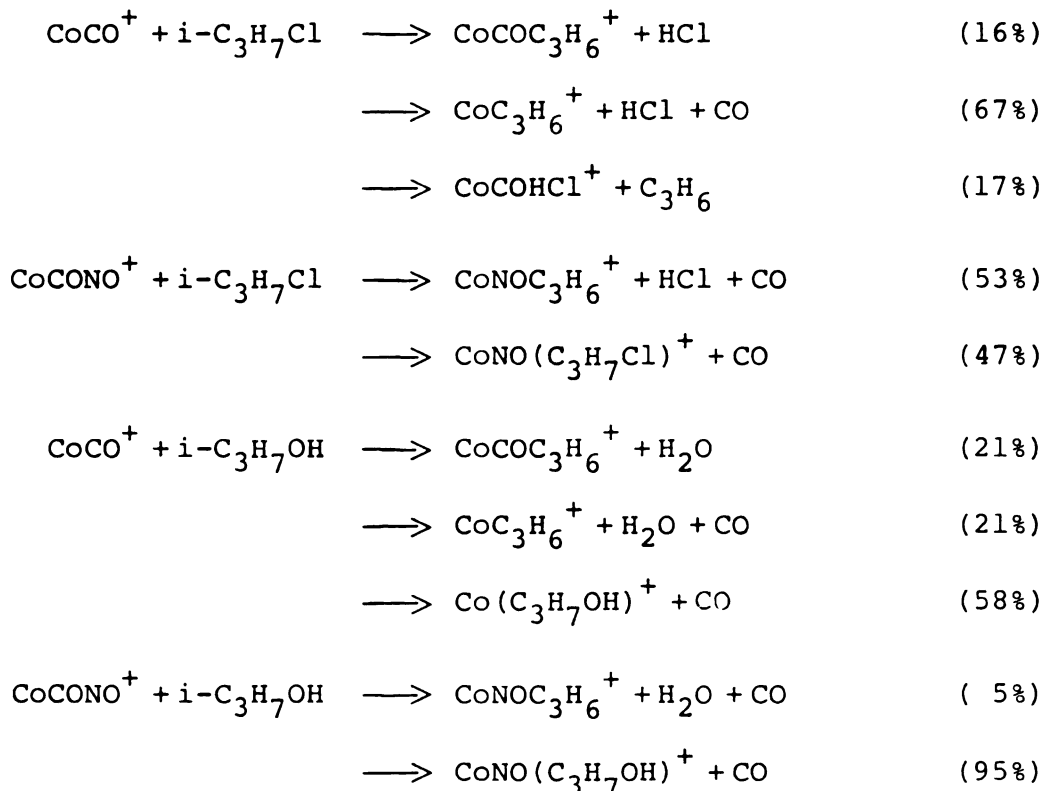
What is surprising is that the tert-butyl cation is not formed (in 2-methyl-2-nitropropane the formation of C_4H_9^+ accounted for 79% of the reactions [6]).

In summary, the reactions of Co^+ with thiols are dominated by insertion into the C-SH bond. In the straight chain butanethiols, the elimination of H_2S and H_2

forming a Co^+ (butadiene) complex also occurs. Insertion of Co^+ into a C-C bond is observed to be a minor pathway in thiols.

B. The Chemistry of $\text{Co}(\text{CO})_x^+$ and $\text{Co}(\text{CO})_y\text{NO}^+$
($x = 1, 2$; $y = 0-3$) Ions with Thiols. Ligand Effects.

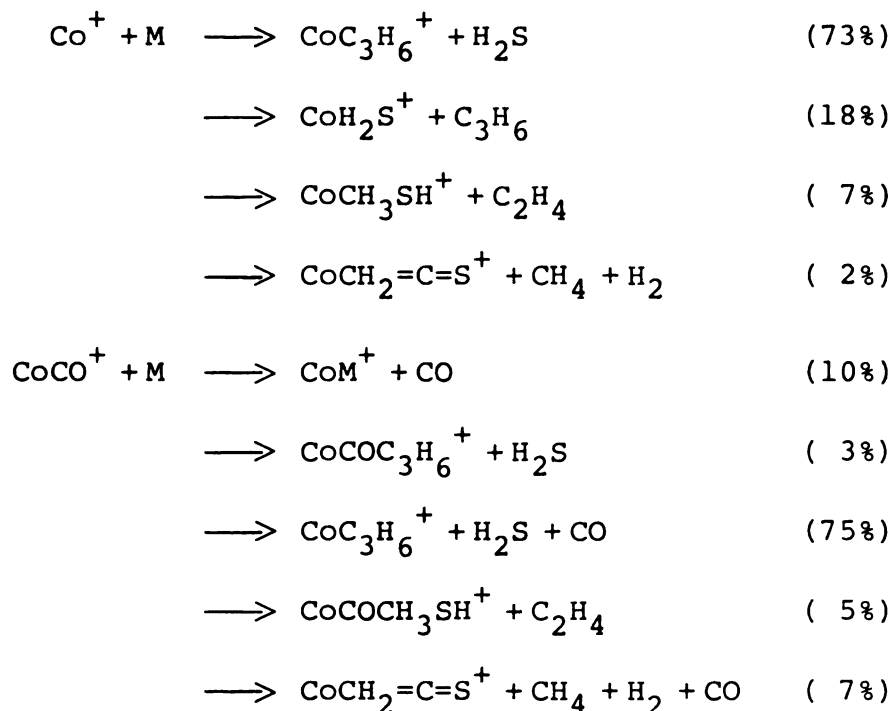
As mentioned earlier, in the electron impact mass spectrum of $\text{Co}(\text{CO})_3\text{NO}$ not only is the bare cobalt ion formed, but other ions containing CO and NO ligands. These ions also react with neutral organic compounds in a way similar to Co^+ . Looking at the chemistry of CoCO^+ and CoCONO^+ with alkyl halides and alcohols we see the similarity with Co^+ [5]:



The last reaction in CoCONO^+ with 2-chloropropane and in CoCO^+ and CoCONO^+ with 2-propanol represent ligand substitution reactions.

The reactions observed for $\text{C}_2\text{-C}_4$ thiols are typical for metal-containing ions, ML_n^+ , in their chemistry with monofunctional organic compounds in the following ways:

(1) The bare metal ion reacts to form the largest variety of products [6]. (2) The organic rearrangement processes observed for CoCO^+ are similar to those observed for Co^+ [4-6,10,11,41]. For example, Co^+ and CoCO^+ show similar reactions with 1-propanethiol ($\text{M}=\text{CH}_3(\text{CH}_2)_2\text{SH}$):



(3) In contrast with the carbonyl ligand, NO ligand deactivates the metal center [4-6,10,11,41]. (Note: only with the propanethiols did CoNO^+ react.) (4) As the

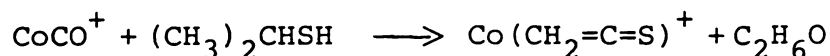
number of ligands present on the metal ion increases what appears to be ligand substitution reactions predominate [6]. In the case of $\text{Co}(\text{CO})_2\text{NO}^+$ reacting with ethanethiol

$$\text{Co}(\text{CO})_2\text{NO}^+ + \text{EtSH} \longrightarrow \text{Co}(\text{CO})_2\text{NO}(\text{EtSH})^{+*} \longrightarrow \text{Co}(\text{CO})\text{NOEtSH}^+ + \text{CO}$$

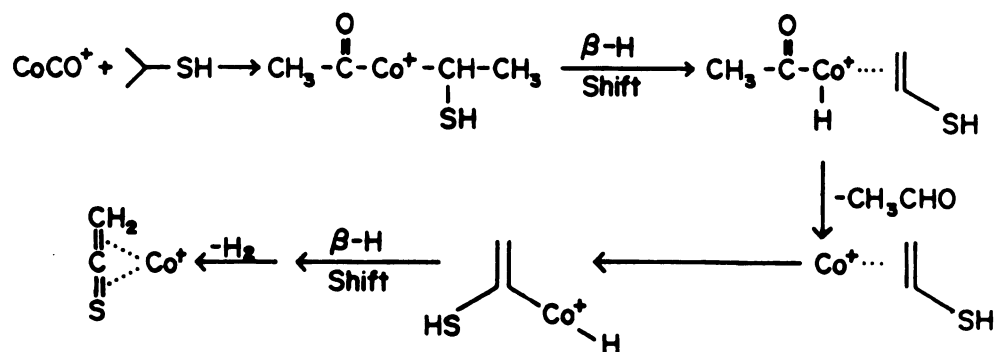
there are no empty orbitals available on the activated complex which can be used to rearrange the ethanethiol. Therefore one can assume that the ethanethiol is still intact in the product ion, i.e., a true ligand substitution.

In the case of CoCO^+ , is the loss of CO occurring from $\text{CoCO}(\text{C}_2\text{H}_5\text{SH})^+$ or from $\text{CoCO}(\text{C}_2\text{H}_4)(\text{H}_2\text{S})^+$? The proton affinities of the different ligands indicate that CO should be lost from either case. (The proton affinity of $\text{C}_2\text{H}_5\text{SH}$ was not available but from the trend observed for H_2S , CH_3SH , H_2O and CH_3OH indicate that the $\text{PA}(\text{C}_2\text{H}_5\text{SH})$ should be greater than $\text{PA}(\text{C}_2\text{H}_5\text{OH})$.) There is no conclusive evidence for just a substitution reaction occurring or if a rearrangement also occurs. For simplicity we will assume that whenever a neutral loss of 28 u occurs, CO only is lost, and the organic molecule is intact on the product ion. One should remember, however, the probability of the molecule remaining intact is reduced for reactions of CoCO^+ , $\text{Co}(\text{CO})_2^+$ and CoCONO^+ due to the availability of empty orbitals on the metal.

In 2-propanethiol, the reactions CoCO^+ are similar to Co^+ . There is the observance of a new reaction in this mixture based upon insertion of CoCO^+ into the C-C bond:



This reaction could occur by metal insertion into the C-C bond, followed by a β -H atom shift and the elimination of CH_4 to give the intermediate $\text{Co}(\text{C}_2\text{H}_3\text{SH})^+$, which then undergoes insertion of Co^+ into a C-H bond and β -H atom shift to yield the $\text{Co}(\text{thioketene})^+$ (similar to scheme VI). However, this reaction is not seen for Co^+ but only for CoCO^- and CoCONO^+ . This implies that the carbonyl actively participates in the chemistry via CoCO^+ insertion into the C-C bond.



As seen from the above mechanism, the neutrals lost are CH_3CHO , and H_2 not CH_4 , H_2 and CO as in 1-propanethiol. Since this reaction occurs with CoCONO^+ and not CoNO^+ further evidence for CoCO^+ insertion is provided.

The insertion of CoCO^+ into the C-C bond is not unprecedented. One example of CoCO^+ insertion has been reported by Radecki and Allison [7]. They have shown that CoCO^+ inserts into the C-C bond of ethyl amine to give $\text{CoCH}_3\text{NH}_2^+$ as the product ion [7].

$$\text{CoCO}^+ + \text{CH}_3\text{CH}_2\text{NH}_2 \longrightarrow \text{CH}_3\text{CO}-\text{Co}^+ - \text{CH}_2\text{NH}_2 \longrightarrow (\text{CH}_2=\text{C}=\text{O})\text{Co}^+(\text{CH}_3\text{NH}_2) \longrightarrow \text{CoCH}_3\text{NH}_2^+.$$

In the chemistry of $\text{Co}(\text{CO})_2\text{NO}^+$ with the two propanethiols there is a reaction corresponding to the loss of $m/z = 29$ from the $[\text{Co}(\text{CO})_2\text{NO}(\text{M})^+]^*$ complex. Most likely this product also involves a CoCO^+ insertion. In this case insertion into the S-H bond where the CO prefers to bond to the hydrogen:

$$\text{Co}(\text{CO})_2\text{NO}^+ + \text{C}_3\text{H}_7\text{SH} \longrightarrow \text{C}_3\text{H}_7\text{S}-\text{Co}(\text{NO})\text{CO}^+ - \text{COH} \longrightarrow \text{C}_3\text{H}_7\text{S} - \text{CoCONO}^+ + \text{COH}.$$

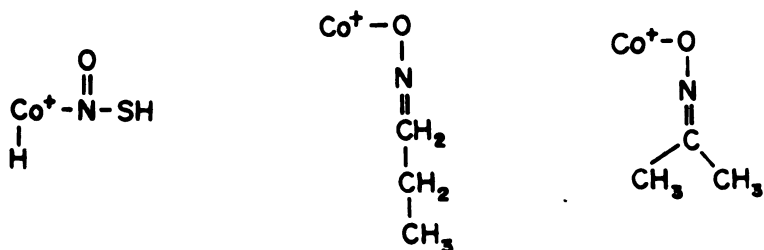
The chemistry of CoNO^+ with organic compounds in general, unique. Either this metal ion does not react at all or it produces reactions that are contradictory to known trends. The "deactivation" may be due to the way the NO ligand bonds to Co^+ . NO may be a one or three electron donor, and if it behaves as a three-electron donor in CoNO^+ , the proper orbitals needed for rearrangements are not present. In the chemistry of CoNO^+ with thiols, the only reactions are observed in the two propanethiols. Both give the same products:

$$\text{CoNO}^+ + \text{C}_3\text{H}_7\text{SH} \longrightarrow \text{CoNOH}_2\text{S}^+ + \text{C}_3\text{H}_6 \longrightarrow \text{CoNOC}_3\text{H}_6^+ + \text{H}_2\text{S}.$$

From the proton affinity/metal-ligand affinities trends thus far observed, one would

expect the olefin to be retained more by the metal but it is the H_2S which is retained more. There are two possible explanations for this phenomenon. First, the ionization potential of the CO ligand is 14.0 eV compared to 7.87 eV for Co, therefore CoCO^+ has the charge retained by the metal, that is, Co^+-CO . However, the ionization potential of the NO is only 9.25 eV, so CoNO^+ may almost look more like $\text{Co}-\text{NO}^+$ than Co^+-NO . Therefore the relative ligand affinities may not be the same because $\text{H}_2\text{S}-\text{Co}$ is formed not $\text{H}_2\text{S}-\text{Co}^+$. (Presently there are not rules for relative ligand affinities for Co.)

The second possible explanation is that instead of Co^+ insertion into the R-SH bond, CoNO^+ insertion into the bond occurs. This is analogous to CoCO^+ insertion processes discussed above. This would then yield product ions of the structure:



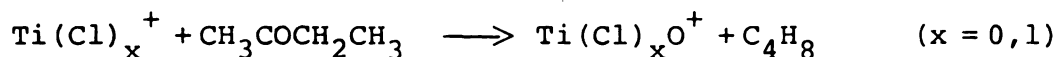
Metal-NO insertions occurring in condensed phases have been discussed in a review by McCleverty [42].

CHAPTER 4

THE CHEMISTRY OF COBALT-CONTAINING IONS WITH BUTANONE AND 3-BUTENONE

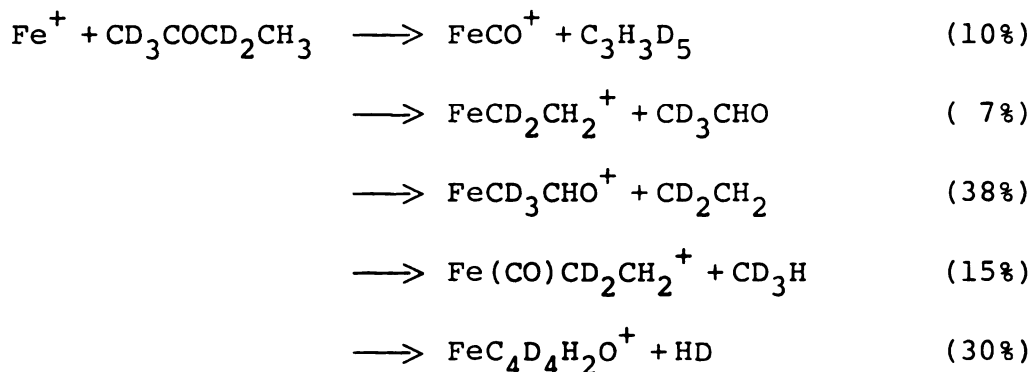
A. The Chemistry of Co^+ with Butanone and 3-Butenone

In the past six years three reports of the gas phase chemistry of transition metal ions with ketones have appeared [39,40,44]. Allison and Ridge [40] have reported the reactions of ions derived from electron impact on TiCl_4 with ketones. Ti^+ and TiCl^+ were observed to reduce aldehydes and small ketones (C_5 or smaller).

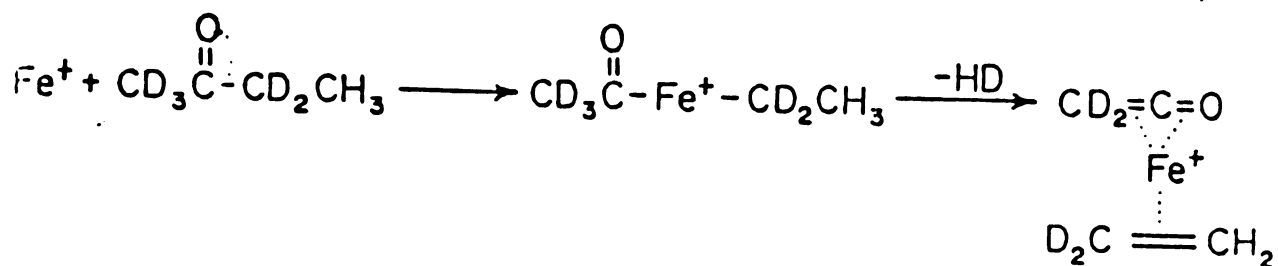


TiCl_2^+ is nonreactive in this mixture, while TiCl_3^+ shows extensive reactions with butanone [40].

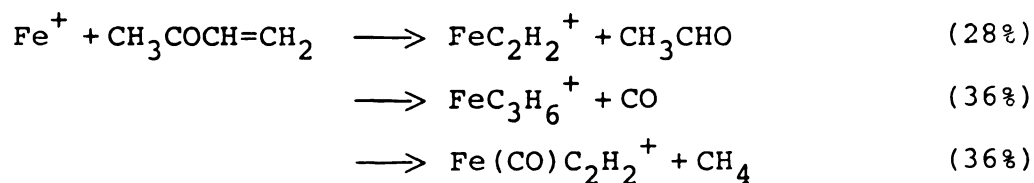
Freiser et al. [39] reported the gas phase chemistry of Fe^+ with aldehydes and ketones. In α, α' - d_5 -butanone, 70% of the reactions involve Fe^+ insertion into either C-CO bond followed by a β -H atom shift or an alkyl shift. The remaining 30% of the reactions involve Fe^+ -induced dehydrogenation of butanone.



In light of newly discovered mechanisms for H_2 elimination, HD elimination may occur either through Fe^+ insertion into a C-D bond followed by a β -H atom shift and the elimination of HD yielding an $\text{Fe}(\text{3-butenone})^+$ complex, (analogous to a metal(butadiene) $^+$ complex), or, insertion of Fe^+ into the CO- CD_2CH_3 bond followed by a 1,4 elimination of HD to give the product:

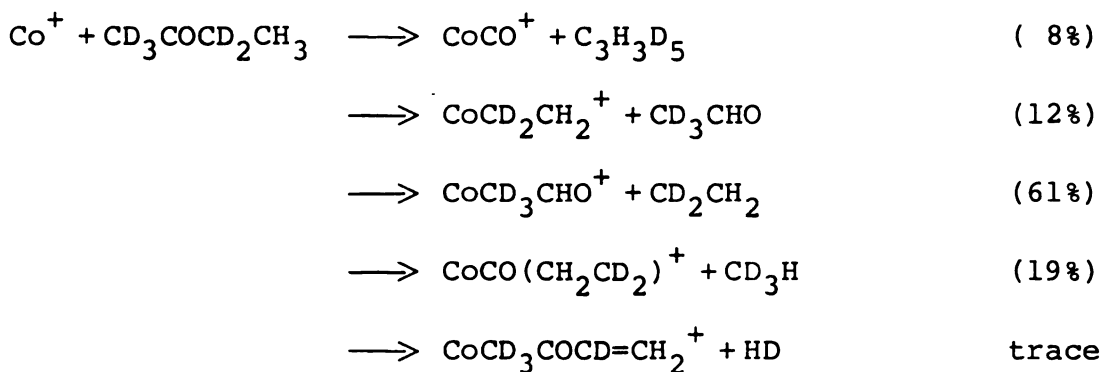


Fe^+ also reacts similarly with 3-butenone.



All of the products in these two Fe^+ -ketone mixtures follow the proton affinity/metal-ligand affinity trends.

Beauchamp et al. [44] have reported similar reactions of Co^+ with butanone, in an atomic ion beam experiment, with a kinetic energy of the reactant ion of ~ 0.5 eV.



1. Butanone

In Table 8 are the reactions of each metal ion with butanone as well as the branching ratios.

The initial interaction of Co^+ with butanone is most likely at the oxygen atom, to give an activated species

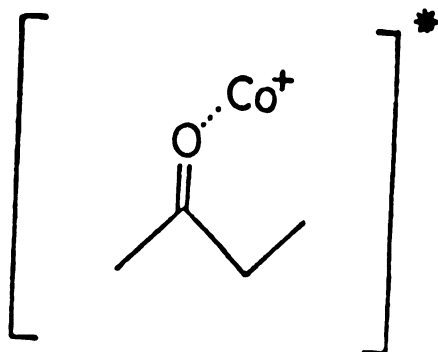
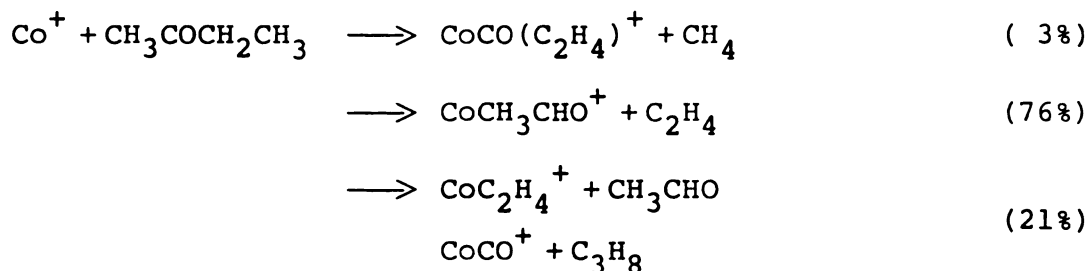


Table 8. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with butanone ($\text{M} = \text{CH}_3\text{COCH}_2\text{CH}_3$).

$\text{Co}^+ + \text{M} \longrightarrow$	$\text{Co}(\text{CO})\text{C}_2\text{H}_4^+ + \text{CH}_4$	(3%)
	$\text{CoCH}_3\text{CH}=\text{C}=\text{O}^+ + \text{CH}_4$	
\longrightarrow	$\text{CoCH}_3\text{CHO}^+ + \text{C}_2\text{H}_4$	(76%)
\longrightarrow	$\text{CoC}_2\text{H}_4^+ + \text{CH}_3\text{CHO}$	(21%)
	$\text{CoCO}^+ + \text{C}_3\text{H}_8$	
$\text{CoCO}^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(90%)
\longrightarrow	$\text{CoCH}_3\text{CHO}^+ + \text{C}_2\text{H}_4 + \text{CO}$	(10%)
$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + 2\text{CO}$	(16%)
\longrightarrow	$\text{CoCOM}^+ + \text{CO}$	(84%)
$\text{CoNO}^+ + \text{M} \longrightarrow$	No Reaction	
$\text{CoCONO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(80%)
\longrightarrow	$\text{CoCONOCH}_3\text{CO}^+ + \text{C}_2\text{H}_5$	(20%)
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(88%)
\longrightarrow	$\text{CoCONOCH}_3\text{CO}^+ + \text{C}_2\text{H}_5 + \text{CO}$	(12%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoCONOM}^+ + 2\text{CO}$	(100%)

which can follow several reaction pathways. The metal ion appears to insert into either C-CO bond in this compound (Scheme IV). The mechanism suggested in Scheme IV is modeled after that proposed by Freiser et al. [39].



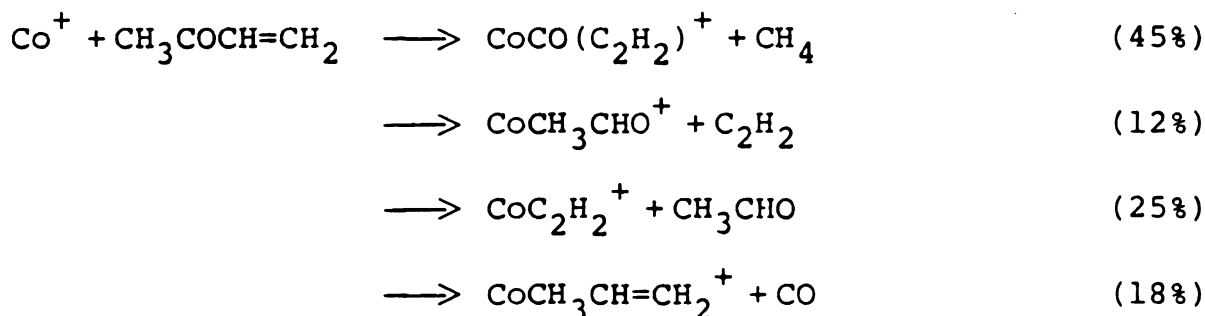
When insertion occurs between the C_2H_5 -CO bond, a β -H shift leads to the complex $\text{Co}(\text{C}_2\text{H}_4)(\text{CH}_3\text{CHO})^+$. From this structure, the ligands undergo competitive elimination to yield the observed products. The proton affinity of the aldehyde is greater than the olefin, therefore the aldehyde should be retained more by the metal ion, as is observed.

When Co^+ inserts into the CH_3 -CO bond, an alkyl shift has been suggested to give structure **XIV**. A β -H atom shift followed by the elimination of the poorer ligand, CH_4 , gives $\text{CoC}_3\text{H}_4\text{O}^+$, which would be in the form $\text{Co}(\text{CO})\text{C}_2\text{H}_4^+$. Elimination of methane can also occur if, after insertion into the CH_3 -CO bond, a β -H shift occurs followed by elimination of CH_4 giving $\text{Co}(\text{CH}_3\text{CH}=\text{C}=\text{O})^+$. From structure **XIV** it is possible to eliminate C_3H_8 to give CoCO^+ ($m/z = 87$). The product CoC_2H_4^+ has the same nominal mass to charge ratio as CoCO^+ .

2. 3-Butenone

Table 9 are the reactions of each metal ion with 3-butenone along with their branching ratios.

3-Butenone reacts with Co^+ similarly to the chemistry observed for butanone:



Co^+ also eliminates CO from 3-butenone giving CoC_3H_6^+ which could be either $\text{Co}(\text{propene})^+$ or $\text{CH}_3\text{-Co}^+\text{-C}_2\text{H}_3$. Since the proton affinity of propene is greater than that of CO, either form would be possible. When the analogous pair of ligands are formed, in the case of butanone, CO and propane, the ligand with the lower proton affinity is also lost giving rise to $\text{Co}(\text{CO})^+$ ($m/z = 87$).

B. The Reactions of CoL_n^+ with Butanone and Butenone

The reactions observed for these two ketones are typical for metal containing ions, ML_n^+ , in their chemistry with monofunctional compounds (although butenone is a bifunctional compound, the observed chemistry is that of the ketone group): (1) Co^+ reacts to form the largest

Table 9. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with 3-butenone ($\text{M} = \text{CH}_3\text{COCH}=\text{CH}_2$).

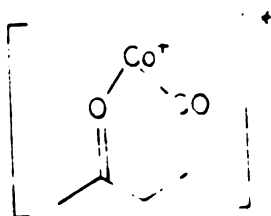
$\text{Co}^+ + \text{M} \longrightarrow$	$\text{Co}(\text{CO})\text{C}_2\text{H}_2^+ + \text{CH}_4$	(45%)
\longrightarrow	$\text{CoCH}_3\text{CHO}^+ + \text{C}_2\text{H}_2$	(12%)
\longrightarrow	$\text{CoC}_2\text{H}_2^+ + \text{CH}_3\text{CHO}$	(26%)
\longrightarrow	$\text{CoC}_3\text{H}_6^+ + \text{CO}$	(18%)
$\text{CoCO}^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(87%)
\longrightarrow	$\text{CoC}_3\text{H}_6^+ + 2\text{CO}$	(3%)
\longrightarrow	$\text{CoCOC}_2\text{H}_2^+ + \text{CH}_3\text{CHO}/$ $\text{CoCOC}_2\text{H}_2^+ + \text{CH}_4 + \text{CO}$	(1%)
\longrightarrow	$\text{CoCOCH}_3\text{CO}^+ + \text{C}_2\text{H}_3$	(7%)
\longrightarrow	$\text{CoCOCH}_3\text{CHO}^+ + \text{C}_2\text{H}_2$	(3%)
$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + 2\text{CO}$	(64%)
\longrightarrow	$\text{CoCOM}^+ + \text{CO}$	(3%)
\longrightarrow	$\text{CoCOCH}_3\text{CO}^+ + \text{C}_2\text{H}_3 + \text{CO}$	(33%)
$\text{CoNO}^+ + \text{M} \longrightarrow$	No Reaction	
$\text{CoCONO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(100%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoCONOM}^+ + 2\text{CO}$	(88%)
\longrightarrow	$\text{CoNOM}^+ + 3\text{CO}$	(12%)

variety of products and (2) as the number of ligands present on the metal ion increases, ligand substitution reactions dominate.

The reactions of $\text{Co}(\text{CO})_2^+$ with butanone show two ligand substitution reactions. This ion complexes with butanone to give $[\text{Co}(\text{CO})_2\text{CH}_3\text{COCH}_2\text{CH}_3]^+$. If this complex then rearranges itself, via reactions similar to Co^+ , to $\text{Co}(\text{CO})_2(\text{CH}_3\text{CHO})(\text{C}_2\text{H}_4)^+$ or $\text{Co}(\text{CO})_2(\text{CH}_4)(\text{CH}_3\text{CH}=\text{C}=\text{O})^+$, the ligand with the lowest proton affinity/metal-ligand affinity should be lost. In the first the CO's have the lowest PA therefore either one or two CO's are lost. In the latter complex CH_4 has the the lowest proton affinity. Therefore one would expect this ligand to be lost. No product corresponding to the loss of CH_4 has been observed in the chemistry of $\text{Co}(\text{CO})_2^+$. Since the CO has the lowest proton affinity of the remaining possible ligands, it is not possible to determine if the product ion contains the intact organic molecule or if it has undergone any rearrangements. As in the case of thiols, for simplicity, one should consider the products losing one or two CO's primarily as ligand substitution.

The reactions of the bare Co^+ ion with butanone require three or four empty orbitals on the metal (see Scheme IV). In CoCO^+ only three orbitals are available. Therefore, the elimination of methane via pathway I, which requires four empty orbitals, cannot occur. In order to

release the excess internal energy of the CoCO^+ -butanone complex



either elimination of CO (ligand substitution reaction) or insertion into the weakest bonds of the ketone occurs. The former process accounts for 90% of the reactions of CoCO^+ .

Insertion into the $\text{CO}-\text{C}_2\text{H}_5$ bond ($D(\text{CH}_3\text{CO}-\text{C}_2\text{H}_4) = 78.9$ kcal/mole) is favored over other C-C bonds, and only the metal center inserts into the C-C bond. That is, the CO remains a spectator in this reaction. After insertion a β -H atom shift and competitive ligand loss occurs to give $\text{CoCH}_3\text{CHO}^+$.

$\text{Co}(\text{CO})_2^+$ undergoes ligand substitution reactions with butanone only (loss of one or two CO's). As expected, CoNO^+ does not react. The NO ligand as previously discussed deactivates the metal center and tends to react with few compounds.

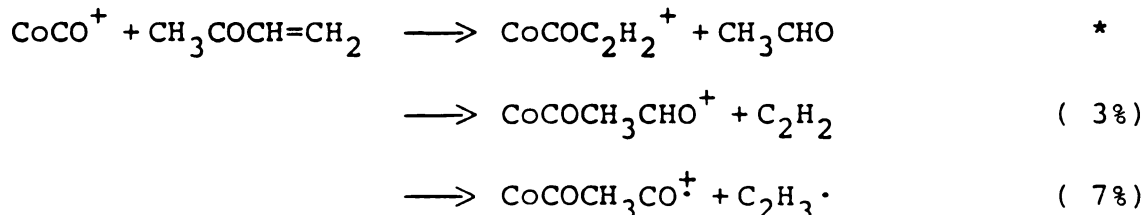
CoCONO^+ and $\text{Co}(\text{CO})_2\text{NO}^+$ react to give the same two products, CoNOM^+ and $\text{CoCONOCH}_3\text{CO}^+$. CoNOM^+ is the result of displacement of one or two CO respectively from CoCONO^+ and $\text{Co}(\text{CO})_2\text{NO}^+$, while the loss of C_2H_5 is via Co^+ insertion

into the weaker C-CO bond. After insertion no orbitals are available for a β -H atom shift. Therefore a bond cleavage occurs. This suggests $D(\text{Co}^+(\text{NO})(\text{CO})-\text{CH}_3\text{CO}) > D(\text{Co}^+(\text{NO})(\text{CO})-\text{C}_2\text{H}_5)$.

$\text{Co}(\text{CO})_3\text{NO}^+$ reacts with butanone via ligand substitution with loss of two carbonyls.

CoCO^+ shows a richer chemistry with butenone than it did with butanone. Ligand substitution still accounts for 87% of the total reactions but more types of rearrangements and bond cleavage processes occur.

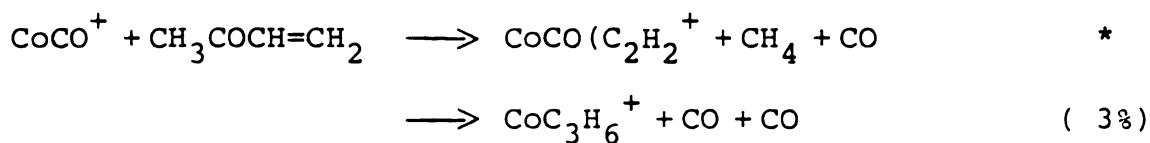
The reactions



involve Co^+ insertion into the $\text{Co}-\text{C}_2\text{H}_3$ bond followed either by a β -H atom shift/competitive elimination process or by bond cleavage. C_2H_2 and CH_3CHO compete better than C_2H_4 and CH_3CHO as noted by the elimination of CH_3CHO .

The other reactions observed between CoCO^+ and butenone involve the loss of the CO ligand first to give Co^+ -butenone complex then insertion into the CH_3 -CO bond, followed by an alkyl shift and elimination of methane or the elimination of CO.

* The product $\text{CoCOC}_2\text{H}_2^+$ is formed by two different pathways; the amount from each could not be determined.



$\text{Co}(\text{CO})_2^+$ reacts with butenone either by ligand substitution or by insertion/bond cleavage. CoNO^+ is nonreactive while $\text{Co}(\text{CO})_x\text{NO}^+$ ions displace one or more CO's. In the chemistry of $\text{Co}(\text{CO})\text{NO}^+$ and $\text{Co}(\text{CO})_2\text{NO}^+$ with butanone there was insertion into the $\text{Co}-\text{C}_2\text{H}_5$ bond followed by bond cleavage with the loss of C_2H_5 . The analogous reaction (loss of C_2H_3) is not observed in 3-butenone primarily because the $\text{Co}-\text{C}_2\text{H}_3$ bond is approximately 9 kcal/mole stronger than the $\text{Co}-\text{C}_2\text{H}_5$ bond in butanone. A second possibility for the lack of C_2H_3 elimination from 3-butenone is that the metal-containing ion may complex strongly with the conjugated system and may prefer to lose CO rather than insert into a C-C bond.

Why is $\text{CH}_2=\text{CHCO}$ lost in the chemistry of $\text{Co}(\text{CO})_2^+$ with 3-butenone and not $\text{CH}_3\text{CH}_2\text{CO}$ in the chemistry of the same ion with butanone? The CH_3-CO bond is slightly weaker in the enone, this may make this bond more accessible to attack.

* The product $\text{CoCOC}_2\text{H}_2^+$ is formed by two different pathways; the amount from each could not be determined.

CHAPTER 5

THE CHEMISTRY OF COBALT CONTAINING IONS WITH UNSUBSTITUTED CARBOXYLIC ACIDS

A. The Chemistry of Co^+ with Unsubstituted Carboxylic Acids

In general, the chemistry of Co^+ with carboxylic acids resembles its chemistry with ketones. That is, the initial sites of attack appear to be bonds on either side of the CO group, which is then followed by either a β -H atom shift or an alkyl shift to the metal.

1. Formic Acid

In Table 10 are the reactions of each metal ion with formic acid along with the branching ratios.

Formic acid, HCOOH , reacts with Co^+ to lose CO. This decarbonylation



reaction involves the Co^+ insertion into the C-OH bond followed by an α -H shift to the metal. Then the weaker ligand is eliminated from the $\text{Co}(\text{CO})\text{H}_2\text{O}^+$ complex. In the

Table 10. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with formic acid ($\text{M} = \text{HCOOH}$).

$\text{Co}^+ + \text{M} \longrightarrow$	$\text{CoH}_2\text{O}^+ + \text{CO}$	(100%)
$\text{CoCO}^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(87%)
	$\longrightarrow \text{CoH}_2\text{O}^+ + 2\text{CO}$	(13%)
$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow$	$\text{CoCOM}^+ + \text{CO}$	(100%)
$\text{CoNO}^+ + \text{M} \longrightarrow$	No Reaction	
$\text{CoCONO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(78%)
	$\longrightarrow \text{CoCONOM}^+ + \text{CO}$	(22%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoCONOM}^+ + 2\text{CO}$	(50%)
	$\longrightarrow \text{Co}(\text{CO})_2\text{NOM}^+ + \text{CO}$	(50%)

ion/molecule reactions of metal ions with organic molecules after the initial insertion of the metal into a bond, a β -H atom shift is usually preferred over other processes (alkyl shifts, α -H shifts, bond cleavages, etc.).

However other processes can occur. For example, Co^+ reacts with methane [8] via insertion into a C-H bond followed by an α -H atom shift with the elimination of H_2 yielding CoCH_2^+ . In ketones, alkyl shifts are frequently observed [39-41]. So in the case of formic acid the α -H shift was not unexpected. Formation of CO and H_2O from formic acid by Co^+ probably does not involve metal insertion into the C-H bond, since an OH shift would have to follow. No evidence for a hydroxyl group shifts has been reported to date. Therefore, one can conclude that insertion into the C-H bond does not occur for formic acid although this is the weakest bond in the molecule. This is due to multiple interactions of the Co^+ with the electron rich oxygen atoms as shown in Scheme V.

2. Acetic Acid

In Table 11 are the reactions of each metal ion with this acid along with the branching ratios.

The chemistry of Co^+ with acetic acid is richer than with formic acid. Besides the decarbonylation reaction, several new reactions are observed (see scheme VI). Following metal insertion into the C-OH bond an alkyl

Scheme V

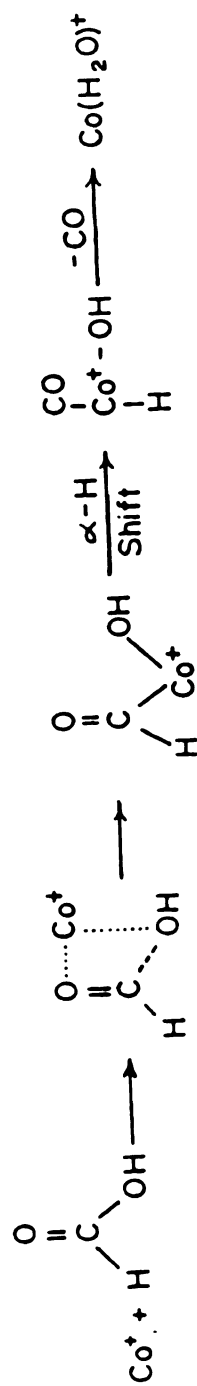
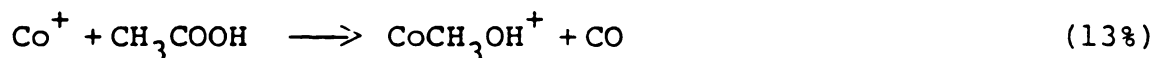


Table 11. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with acetic acid ($\text{M} = \text{CH}_3\text{COOH}$).

Co^+	$+ \text{M} \longrightarrow$	$\text{CoCH}_3\text{OH}^+ + \text{H}_2\text{O}$	(13%)
	\longrightarrow	$\text{CoH}_2\text{O}^+ + \text{CH}_2=\text{C}=\text{O}$	(58%)
	\longrightarrow	$\text{CoCH}_2=\text{C}=\text{O}^+ + \text{H}_2\text{O}$	(21%)
	\longrightarrow	$\text{CoCH}_2\text{O}_2^+ + \text{CH}_2$	(8%)
CoCO^+	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(72%)
	\longrightarrow	$\text{CoCOH}_2\text{O}^+ + \text{CH}_2=\text{C}=\text{O}$	(6%)
	\longrightarrow	$\text{Co}(\text{CO})(\text{HCOOH})^+ + \text{CH}_2$	(11%)
	\longrightarrow	$\text{CoCH}_2=\text{C}=\text{O}^+ + \text{H}_2\text{O} + \text{CO}$	(6%)
	\longrightarrow	$\text{CoCOCH}_2=\text{C}=\text{O}^+ + \text{H}_2\text{O}$	(5%)
$\text{Co}(\text{CO})_2^+$	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + 2\text{CO}$	(5%)
	\longrightarrow	$\text{CoCOM}^+ + \text{CO}$	(95%)
CoNO^+	$+ \text{M} \longrightarrow$	$\text{CoNOH}_2\text{O}^+ + \text{CH}_2=\text{C}=\text{O}$	(100%)
CoCONO^+	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(92%)
	\longrightarrow	$\text{CoNOCH}_2=\text{C}=\text{O}^+ + \text{H}_2\text{O} + \text{CO}$	(8%)
$\text{Co}(\text{CO})_2\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(78%)
	\longrightarrow	$\text{CoCONOM}^+ + \text{CO}$	(22%)
$\text{Co}(\text{CO})_3\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoCONOM}^+ + 2\text{CO}$	(75%)
	\longrightarrow	$\text{Co}(\text{CO})_2\text{NOM}^+ + \text{CO}$	(25%)

shift can occur to give CoCH_3OH^+ , or a β -H shift can occur giving the $\text{Co}(\text{H}_2\text{O})(\text{ketene})^+$ intermediate. From this intermediate Co^+ can retain either ligand, in this case preferring to retain the water. Also Co^+ can insert into the C-C bond of the ketene to eliminate CH_2 :



Co^+ can also insert into the CH_3 -CO bond, followed by an α -H shift to give intermediate and then eliminate CH_2 : to give $\text{Co}(\text{HCOOH})^+$. While loss of CH_2 : may appear to be an unlikely process, it is a minor product. Also, CH_2 : elimination in such reactions is not unprecedented. Freiser, Cassady, McElvany and Allison [6] reported the elimination of CH_2 : from small nitroalkanes by Co^+ to be a minor pathway (<3%). Also, Babinec and Allison reported the elimination of CH_2 : accounted for 4% of the reactions of Fe^+ with 1-aminopropane [45].

3. Propanoic Acid

In Table 12 are the reactions of each metal ion with propanoic acid along with the branching ratios.

Table 12. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with propanoic acid ($\text{M} = \text{CH}_3\text{CH}_2\text{COOH}$).

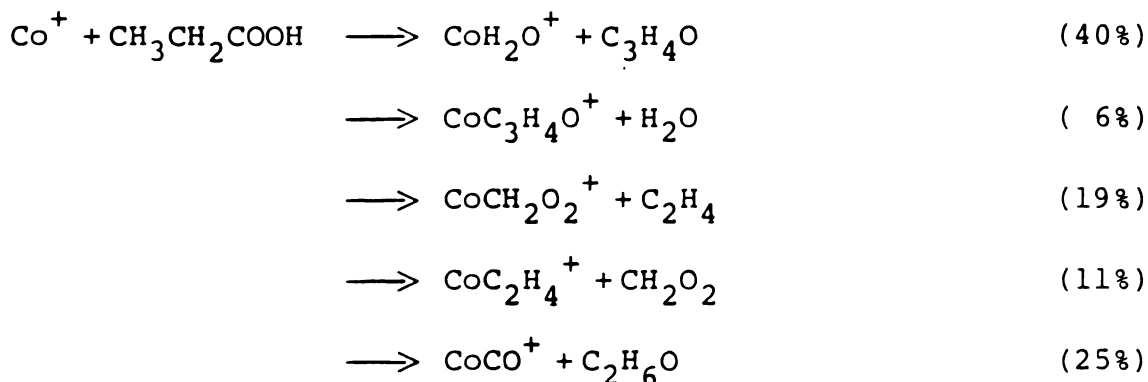
$\text{Co}^+ + \text{M} \longrightarrow$	$\text{CoCO}^+ + \text{C}_2\text{H}_4 + \text{H}_2\text{O}$	(25%)
\longrightarrow	$\text{CoH}_2\text{O}^+ + \text{CH}_3\text{CH}=\text{C}=\text{O}$	(40%)
\longrightarrow	$\text{CoCH}_3\text{CH}=\text{C}=\text{O}^+ + \text{H}_2\text{O}$	(6%)
\longrightarrow	$\text{CoHCOOH}^+ + \text{C}_2\text{H}_4$	(19%)
	$\text{Co}(\text{CO})\text{H}_2\text{O}^+ + \text{C}_2\text{H}_4$	
\longrightarrow	$\text{CoC}_2\text{H}_4^+ + \text{HCOOH}$	(11%)
	$\text{CoC}_2\text{H}_4^+ + \text{H}_2\text{O} + \text{CO}$	
$\text{CoCO}^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(80%)
\longrightarrow	$\text{CoCH}_3\text{CH}_2\text{OH}^+ + 2\text{CO}$	(6%)
	$\text{CoC}_2\text{H}_4(\text{H}_2\text{O})^+ + 2\text{CO}$	
\longrightarrow	$\text{CoCOH}_2\text{O}^+ + \text{CH}_3\text{CH}=\text{C}=\text{O}$	(5%)
	$\text{CoHCOOH}^+ + \text{C}_2\text{H}_4 + \text{CO}$	
\longrightarrow	$\text{CoH}_2\text{O}^+ + \text{CH}_3\text{CH}=\text{C}=\text{O} + \text{CO}$	(9%)
$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow$	$\text{CoCOM}^+ + \text{CO}$	(88%)
\longrightarrow	$\text{CoM}^+ + 2\text{CO}$	(5%)
\longrightarrow	$\text{CoCOH}_2\text{O}^+ + \text{CH}_3\text{CH}=\text{C}=\text{O} + \text{CO}$	(7%)
$\text{CoNO}^+ + \text{M} \longrightarrow$	$\text{CoNOH}_2\text{O}^+ + \text{CH}_3\text{CH}=\text{C}=\text{O}$	(100%)
$\text{CoCONO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(85%)
\longrightarrow	$\text{CoNOH}_2\text{O}^+ + \text{CH}_3\text{CH}=\text{C}=\text{O} + \text{CO}$	(15%)

Table 12 Continues.

Table 12 Continued.

$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M}$	\longrightarrow	$\text{CoNOM}^+ + 2\text{CO}$	(60%)
	\longrightarrow	$\text{CoNOH}_2\text{O}^+ + \text{CH}_3\text{CH}=\text{C}=\text{O}$	(40%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M}$	\longrightarrow	$\text{CoCONOM}^+ + 2\text{CO}$	(89%)
	\longrightarrow	$\text{Co}(\text{CO})_2\text{NOM}^+ + \text{CO}$	(11%)

Many of the reactions of propanoic acid (see scheme VII) with Co^+ are similar to those observed with acetic acid. One noticeable exception is that $\text{Co}(\text{CH}_3\text{CH}_2\text{OH})^+$, i.e. loss of CO is not observed. What is observed, however, is a series of products $\text{Co}(\text{CO})(\text{H}_2\text{O})^+$, CoC_2H_4^+ , CoH_2O^+ and CoCO^+ . (Note: in order to distinguish CoC_2H_4^+ from CoCO^+ ($m/z = 87$) deuterated propanoic acid (d_6) was used. All hydrogen containing products are given as hydrogen atoms and not deuterium.) This suggests that metal insertion/alkyl shift mechanism occurs to give ethanol as a ligand, but then the ethanol undergoes the reactions typical of alcohols (i.e. the formation of H_2O and ethene).



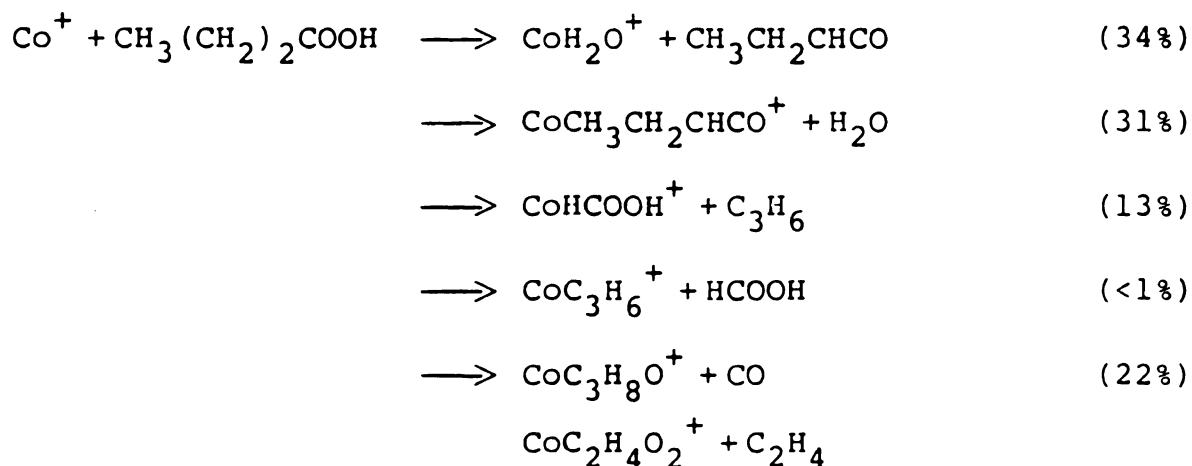
Co^+ also inserts into the C-CO bond in propanoic acid, a β -H atom shift leads to the $\text{Co}(\text{ethene})(\text{HCOOH})^+$ complex. Competitive elimination of the ligands occurs. The reactions above are given for the ionic and neutral products regardless of the stoichiometry. All of the products formed in this mixture occur by at least two

independent pathways, therefore, the proposed structures for the product ions are given in scheme VII. The branching ratios calculated represent the extent of a given product being formed regardless of the pathway.

4. Butanoic Acid

In Table 13 are the reactions of each metal ion with this acid along with the branching ratios.

Butanoic acid exhibits reactions with Co^+ (see scheme VIII) similar to those observed with propanoic acid. In this mixture, a product ion of $m/z = 119$ is observed.



This corresponds to an ion with the formula $\text{CoC}_3\text{H}_8\text{O}^+$ or $\text{CoC}_2\text{H}_4\text{O}_2^+$. This discussion will assume both are present since both are reasonable based on previously discussed mechanisms. Regarding the ion of formula $\text{CoC}_3\text{H}_8\text{O}^+$, this ion may be $\text{Co}(\text{l-propanol})^+$ due to insertion into the CO-OH bond followed by an alkyl shift and loss of CO, or it may

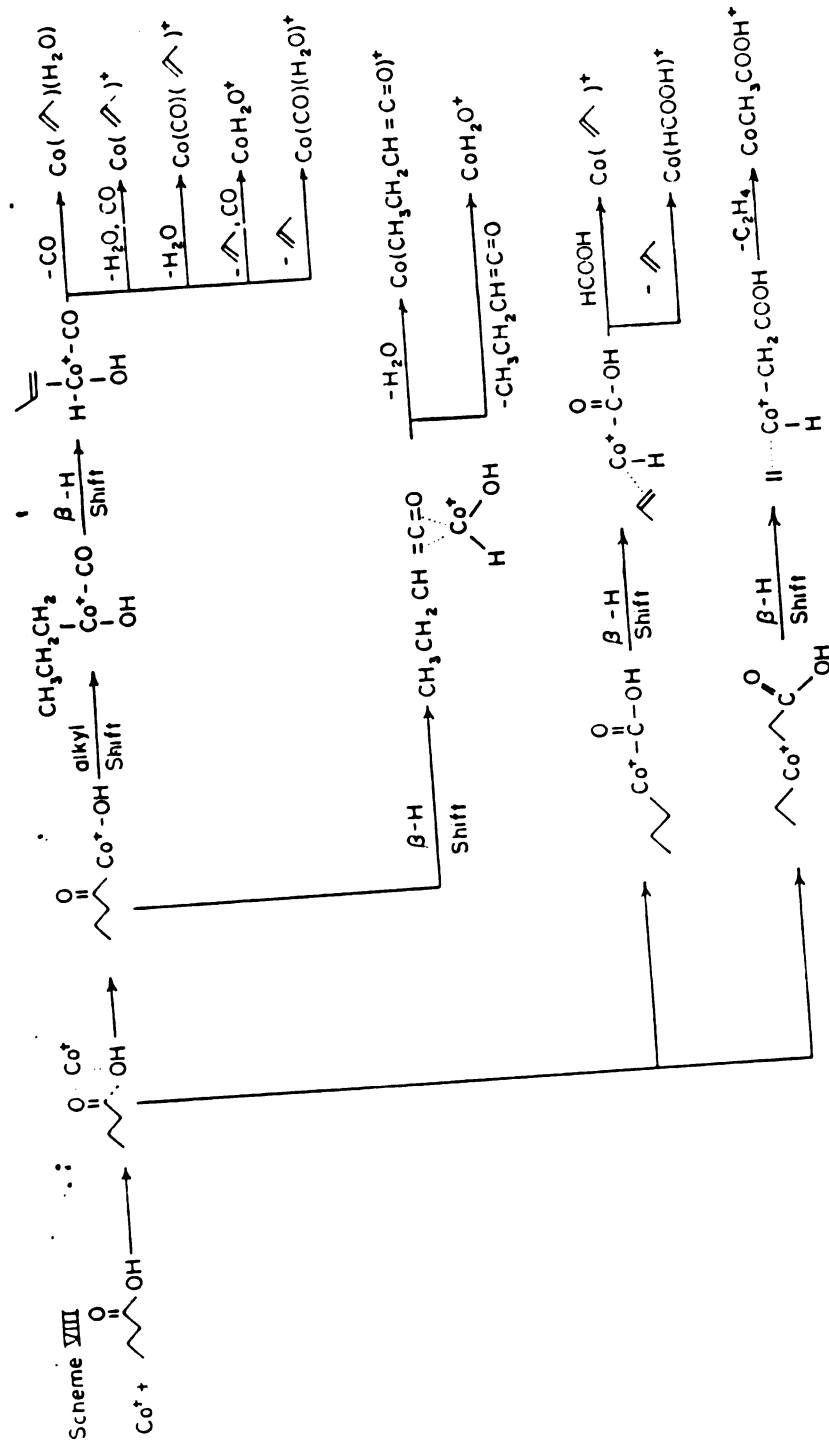
Table 13. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with butanoic acid ($\text{M} = \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$).

$\text{Co}^+ + \text{M} \longrightarrow$	$\text{CoH}_2\text{O}^+ + \text{CH}_3\text{CH}_2\text{CH}=\text{C}=\text{O}$	(34%)
\longrightarrow	$\text{CoCH}_3\text{CH}_2\text{CH}=\text{C}=\text{O}^+ + \text{H}_2\text{O}$	(31%)
\longrightarrow	$\text{CoHCOOH}^+ + \text{C}_3\text{H}_6 /$ $\text{Co}(\text{CO})\text{H}_2\text{O}^+ + \text{C}_3\text{H}_6$	(13%)
\longrightarrow	$\text{CoC}_3\text{H}_6^+ + \text{HCOOH} /$ $\text{CoC}_3\text{H}_6^+ + \text{CO} + \text{H}_2\text{O}$	(<1%)
\longrightarrow	$\text{CoCH}_3\text{CH}_2\text{CH}_2\text{OH}^+ + \text{CO} /$ $\text{Co}(\text{C}_3\text{H}_6)\text{H}_2\text{O} + \text{CO} /$ $\text{CoCH}_3\text{COOH}^+ + \text{C}_2\text{H}_4$	(22%)
$\text{CoCO}^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(27%)
\longrightarrow	$\text{CoCOH}_2\text{O}^+ + \text{CH}_3\text{CH}_2\text{CH}=\text{C}=\text{O}$ $\text{CoHCOOH}^+ + \text{C}_3\text{H}_6 + \text{CO}$	(9%)
\longrightarrow	$\text{CoH}_2\text{O}^+ + \text{CH}_3\text{CH}_2\text{CH}=\text{C}=\text{O}$	(45%)
\longrightarrow	$\text{CoCH}_3\text{COOH}^+ + \text{C}_2\text{H}_4 + \text{CO} /$ $\text{CoCH}_3\text{CH}_2\text{CH}_2\text{OH}^+ + 2\text{CO}$ $\text{CoC}_3\text{H}_6(\text{H}_2\text{O})^+ + 2\text{CO}$	(8%)
\longrightarrow	$\text{CoCOHCOOH}^+ + \text{C}_3\text{H}_6$	(5%)
\longrightarrow	$\text{CoCOCH}_3\text{CH}_2\text{COOH}^+ + \text{CH}_2$	(6%)
$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow$	$\text{CoCOM}^+ + \text{CO}$	(40%)
\longrightarrow	$\text{CoM}^+ + 2\text{CO}$	(5%)
\longrightarrow	$\text{Co}(\text{CO})_2\text{H}_2\text{O}^+ + \text{CH}_3\text{CH}_2\text{CH}=\text{C}=\text{O}$	(55%)
$\text{CoNO}^+ + \text{M} \longrightarrow$	$\text{CoNOCH}_3\text{CH}_2\text{CH}=\text{C}=\text{O}^+ + \text{H}_2\text{O}$	(100%)

Table 13 Continues.

Table 13 Continued.

$\text{CoCONO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(35%)
\longrightarrow	$\text{CoNOCH}_3\text{CH}_2\text{CH}=\text{C}=\text{O}^+ + \text{H}_2\text{O} + \text{CO}$	(2%)
\longrightarrow	$\text{CoNOH}_2\text{O}^+ + \text{CH}_3\text{CH}_2\text{CH}=\text{C}=\text{O}$	(63%)
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(100%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoCONOM}^+ + 2\text{CO}$	(64%)
\longrightarrow	$\text{Co}(\text{CO})_2\text{NOM}^+ + \text{CO}$	(36%)



have the structure $\text{Co}(\text{propene})(\text{H}_2\text{O})^+$. Since products corresponding to CoH_2O^+ , CoCOH_2O^+ and CoC_3H_6^+ are also observed, this ion most likely has the latter structure. This is also consistent with what is observed in the propanoic acid reactions. For the formula $\text{CoC}_2\text{H}_4\text{O}_2^+$, this product can be formed by Co^+ insertion into the $\text{C}_2\text{-C}_3$ bond followed by a $\beta\text{-H}$ shift and then competitive elimination from the intermediate $(\text{C}_2\text{H}_4)\text{Co}^+(\text{CH}_3\text{COOH})$ yielding $\text{CoCH}_3\text{COOH}^+$. It has been observed in other studies [10,46] that as the alkyl chain length increases more alkane like chemistry occurs, i.e. insertion into the C-C bonds occur with increasing frequency in addition to insertion into C-CO and Co-OH bonds. This may be what occurs in this compound. In order to resolve this ambiguity, future experiments could be performed using deuterated butanoic acid (d_7), or collision induced dissociation (CID) experiments could be used to determine the product ion structure.

5. 3-Butenoic Acid

In Table 14 are the reactions of each metal ion with this acid along with the branching ratios.

The presence of the C-C double bond conjugated with the C=O bond system severely reduced the chemistry of Co^+ with acids. In trans-2-butenic acid,

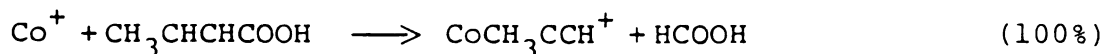
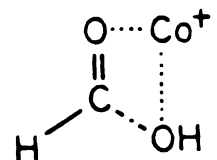


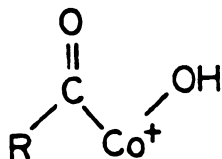
Table 14. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with 2-butenic acid ($\text{M} = \text{CH}_3\text{CH}=\text{CHCOOH}$).

$\text{Co}^+ + \text{M} \longrightarrow$	$\text{CoCH}_3\text{C}\equiv\text{CH}^+ + \text{HCOOH}$	(100%)
$\text{CoCO}^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + 2\text{CO}$	(32%)
	$\longrightarrow \text{CoCOM}^+ + \text{CO}$	(68%)
$\text{CoNO}^+ + \text{M} \longrightarrow$	No Reaction	
$\text{CoCONO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(100%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoCONOM}^+ + 2\text{CO}$	(90%)
	$\longrightarrow \text{Co}(\text{CO})_2\text{NOM}^+ + \text{CO}$	(10%)

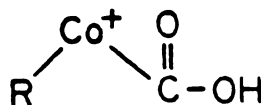
the only product observed is CoC_3H_4^+ . For acids such as formic acid the Co^+ interacts with the CO and the OH at the same time.



This interaction weakens the Co-OH bond, which is then most susceptible to Co^+ insertion. Because of this structure **XVI** is preferred over structure **XVII**.

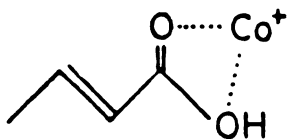


XVI

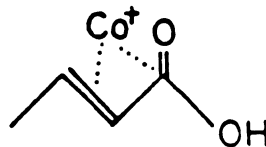


XVII

But in trans-2-butenic acid the Co^+ has two possibilities:



XVIII



XIX

From the observed reaction, the latter structure is preferred. Earlier in our discussion of the proton affinity/metal ligand affinity we noted that Co^+ preferred to retain the olefin over H_2O . This serves as further evidence that the latter structure is the initial Co^+ -acid

complex. From this complex, Co^+ can easily insert into the CO-C bond followed by a β -H atom shift and the elimination of formic acid.

6. 2,2-Dimethylpropanoic Acid

In Table 15 are the reactions of each metal ion in this mixture along with the branching ratios.

2,2-Dimethylpropanoic acid does not react with Co^+ . Note that if insertion of the Co^+ ion into the C-OH bond occurred there are no hydrogens in the position to shift onto the metal. An alkyl shift is also unlikely since this process decreases as the chain length and branching increases. Therefore a kinetic factor may account for the lack of formation of CoCO^+ and $\text{Co}(\text{tert-butanol})^+ / \text{Co}(\text{H}_2\text{O})(2\text{-methylpropene})^+$.

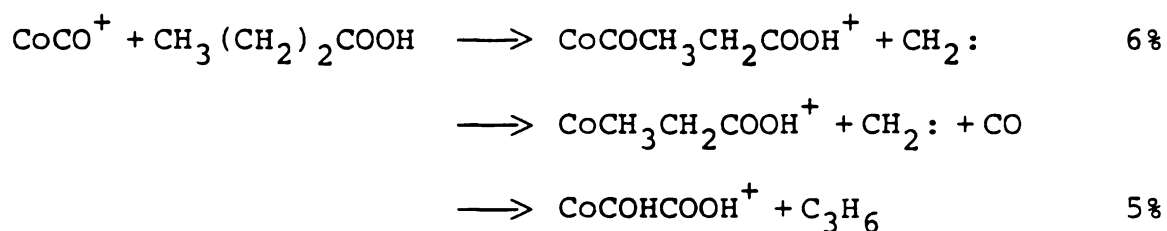
Also Co^+ insertion into the C-COOH bond may not occur due to the steric hinderance of the bulky tert-butyl group.

7. Ligand Effects

The reactions of CoL_n^+ with carboxylic acids, as also observed for thiols and butanone, are typical for monofunctional compounds also. CoCO^+ reacts for the most part like Co^+ with all of the unsubstituted acids studied. The only new reactions occur in butanoic acid.

Table 15. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with
2,2-dimethylpropanoic acid ($\text{M} = (\text{CH}_3)_3\text{CCOOH}$).

Co^+	$+ \text{M} \longrightarrow$	No Reaction	
CoCO^+	$+ \text{M} \longrightarrow$	CoM^+	(100%)
$\text{Co}(\text{CO})_2^+$	$+ \text{M} \longrightarrow$	$\text{CoCOM}^+ + \text{CO}$	(94%)
	\longrightarrow	$\text{CoM}^+ + 2\text{CO}$	(6%)
CoNO^+	$+ \text{M} \longrightarrow$	No Reaction	
CoCONO^+	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(100%)
$\text{Co}(\text{CO})_3\text{NO}^+$	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + 3\text{CO}$	(90%)
	\longrightarrow	$\text{CoNOCOC}_3\text{H}_5^+ + \text{CO} + \text{COOH}$	(10%)



Initially one would assume that CoCO^+ inserts into the $\text{C}_3\text{-C}_4$ bond followed by a $\beta\text{-H}$ atom shift to the metal to give $\text{Co}(\text{CH}_3\text{CH}_2\text{COOH})(\text{CH}_2\text{CO})^+$, but $\text{CH}_2:$ is lost either alone or with the loss of CO. If CO partakes in the reaction it should always be eliminated. In this case where CoL_n^+ induces a new reaction but not because of ligand participation. What may induce this reaction to occur is that when CoCO^+ complexes with the acid a higher energy species is formed than with Co^+ only, therefore higher energetic reactions may occur [41,46].

A horizontal trend (a trend observed as alkyl group increases in size) is observed in the chemistry of CoNO^+ . In acetic and propanoic acids, CoNO^+ reacts via insertion of Co^+ into the C-OH bond/ $\beta\text{-H}$ atom shift mechanism to give $\text{CoNO}(\text{ketene})(\text{H}_2\text{O})^+$ which then loses the ketene and retains the H_2O . When CoNO^+ reacts with butanoic acid (via the same mechanism) water is eliminated. After the initial reaction to give $\text{CoNO}(\text{H}_2\text{O})(\text{ethylketene})^+$ the metal center, Co^+ (of CoNO^+), inserts into the $\text{C}_2\text{H}_5\text{---CH=C=O}$ bond, followed by a $\beta\text{-H}$ atom shift to give $\text{CoNO}(\text{H}_2\text{O})(\text{C}_2\text{H}_4)(\text{CH}_2=\text{C=O})^+$ which then loses the poorest ligand, H_2O , to give $\text{CoNO}(\text{C}_2\text{H}_4)(\text{CH}_2=\text{C=O})^+$. The retention of water in the

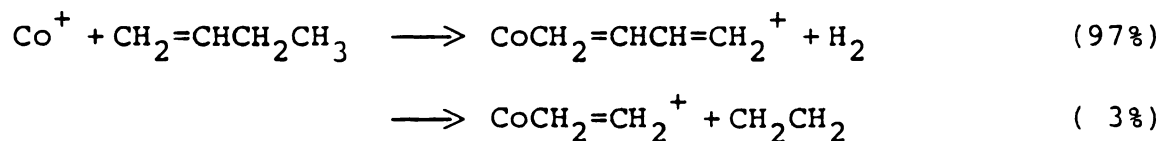
smaller acids parallels what was observed in the thiols and CoNO^+ , that is, the ligand with the smaller proton affinity is retained.

As discussed in the previous chapters, whenever a reaction occurs where a carbonyl is the only elimination product, the structure of the product ion has to be determined. Is the product in the form of CoM^+ , where M is the intact molecule, or is in the form Co(A)(B)^+ , where A and B represent ligand structures based upon rearrangement of the acid. In the carboxylic acids, all possible rearrangement fragments have proton affinities (therefore, metal-ligand affinities) higher than CO. Therefore, in each case, the CO should be lost. In ions such as Co(CO)_x^+ ($x = 1, 2$) and CoCONO^+ when CO is lost there is a good probability that the product is a mixture of CoM^+ and Co(A)(B)^+ , while in the $\text{Co(CO)}_{2,3}\text{NO}^+$ the parent molecule most likely is intact because of lack of empty orbitals on the metal.

CHAPTER 6

THE CHEMISTRY OF COBALT CONTAINING IONS WITH ALLYL-X COMPOUNDS

The five compounds whose chemistries are reported in this chapter contain neighboring functional groups where one group is a double bond. Armentrout and Beauchamp have reported the chemistry of Co^+ with alkenes [9]. At thermal energies, no exothermic reactions occur between Co^+ and propene. 1-Butene reacts predominantly by H_2 elimination (97%) with some ethene elimination (3%).



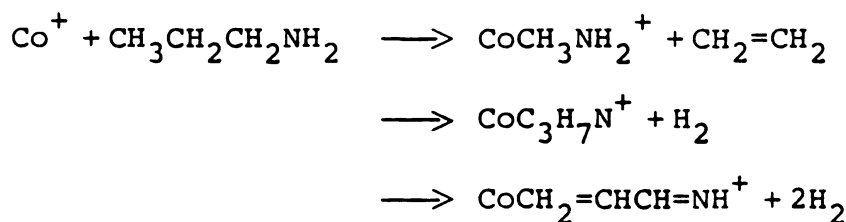
Elimination of H_2 occurs with butenes much more extensively than other olefins, presumably because of the stable butadiene complex which is formed as a product.

One object of this work is to determine whether these allyl-X compounds give products typical of olefins and/or X-containing species.

A. The Chemistry of the Cobalt Ion with Allyl Compounds

In Tables 16-20 are the reactions for each metal ion with the different allyl compounds. Also given are the branching ratios.

n-Propylamine reacts with Co^+ as follows [7]:



Amines are atypical of polar saturated organic compounds (such as alcohols) in their gas phase chemistry with transition metal ions in that metal insertion into the polar C-N bond apparently does not occur [7]. Amines actually react analogously to alkanes—i.e. via H_2 (insertion into C-H bond) and alkene elimination (insertion into C-C bond). Similar products are observed with allyl amine. Both allyl amine and n-propylamine react to form CH_5N^+ and $\text{CoC}_3\text{H}_5\text{N}^+$. In the case of allyl amine, one does see strong evidence for insertion of Co^+ into the C-N bond:

Table 16. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with allyl amine ($\text{M} = \text{CH}_2=\text{CHCH}_2\text{NH}_2$).

$\text{Co}^+ + \text{M} \longrightarrow$	$\text{CoC}_3\text{H}_4^+ + \text{NH}_3$	(14%)
\longrightarrow	$\text{CoC}_3\text{H}_5^+ + \text{N}_4$	(7%)
\longrightarrow	$\text{CoCH}_2=\text{CHCH}=\text{NH}_2^+ + \text{H}_2$	(43%)
\longrightarrow	$\text{CoCH}_3\text{NH}_2^+ + \text{C}_2\text{H}_2$	(36%)
$\text{CoCO}^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(37%)
\longrightarrow	$\text{CoC}_3\text{H}_4^+ + \text{NH}_3 + \text{CO}$	(8%)
\longrightarrow	$\text{CoC}_3\text{H}_5^+ + \text{NH}_2 + \text{CO}$	(4%)
\longrightarrow	$\text{CoCOC}_3\text{H}_5^+ + \text{NH}_2$	(1%)
\longrightarrow	$\text{CoCH}_2=\text{CHCH}=\text{NH}^+ + \text{H}_2 + \text{CO}$	(28%)
\longrightarrow	$\text{CoCH}_3\text{NH}_2^+ + \text{C}_2\text{H}_2 + \text{CO}$	(15%)
\longrightarrow	$\text{CoCOCH}_3\text{NH}_2^+ + \text{C}_2\text{H}_2$	(7%)
$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow$	$\text{CoCOM}^+ + \text{CO}$	(59%)
\longrightarrow	$\text{Co}(\text{CO})_2\text{NH}_3^+ + \text{C}_3\text{H}_4$	(12%)
\longrightarrow	$\text{Co}(\text{CO})_2\text{C}_3\text{H}_5^+ + \text{NH}_2$	(29%)
$\text{CoNO}^+ + \text{M} \longrightarrow$	No Reaction	
$\text{CoCONO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(100%)

Table 16 Continues.

Table 16 Continued.

$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 2\text{CO}$	(74%)
	$\longrightarrow \text{CoNOCH}_3\text{NH}_2^+ + \text{C}_2\text{H}_2 + \text{CO}$	(17%)
	$\longrightarrow \text{CoCONONH}_3^+ + \text{C}_3\text{H}_4 + \text{CO}$	(3%)
	$\longrightarrow \text{Co}(\text{CO})_2\text{NONH}_3^+ + \text{C}_3\text{H}_4$	(6%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 3\text{CO}$	(86%)
	$\longrightarrow \text{CoCONONH}_3^+ + \text{C}_3\text{H}_4 + 2\text{CO}$	(3%)
	$\longrightarrow \text{Co}(\text{CO})_2\text{NONH}_3^+ + \text{C}_3\text{H}_4 + \text{Co}$	(11%)

Table 17. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with
1-chloro-2-propene ($\text{M} = \text{CH}_2=\text{CHCH}_2\text{Cl}$).

$\text{Co}^+ + \text{M} \longrightarrow \text{CoC}_3\text{H}_4^+ + \text{HCl}$	(100%)
$\text{CoCO}^+ + \text{M} \longrightarrow \text{CoM}^+ + \text{CO}$	(74%)
$\longrightarrow \text{CoC}_3\text{H}_4^+ + \text{HCl} + \text{CO}$	(26%)
$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow \text{CoM}^+ + 2\text{CO}$	(100%)
$\text{CoNO}^+ + \text{M} \longrightarrow \text{No Reaction}$	
$\text{CoCONO}^+ + \text{M} \longrightarrow \text{CoNOM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow \text{CoNOM}^+ + 2\text{CO}$	(100%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow \text{CoCONOM}^+ + 2\text{CO}$	(100%)

Table 18. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with
1-bromo-2-propene ($\text{M} = \text{CH}_2=\text{CHCH}_2\text{Br}$).

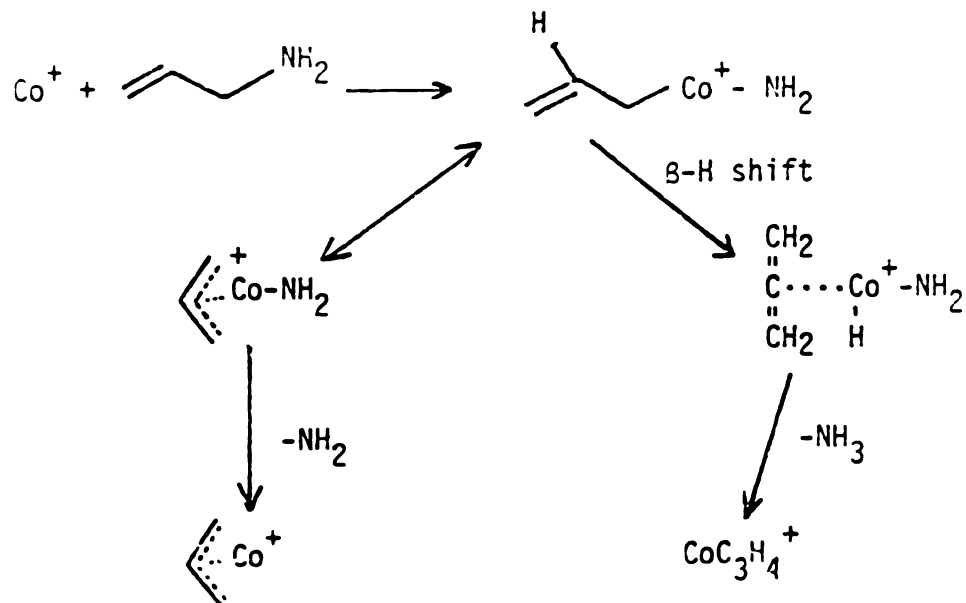
$\text{Co}^+ + \text{M} \longrightarrow \text{CoC}_3\text{H}_4^+ + \text{HBr}$	(73%)
$\longrightarrow \text{CoC}_3\text{H}_5^+ + \text{Br}$	(10%)
$\longrightarrow \text{CoBr}^+ + \text{C}_3\text{H}_5$	(17%)
$\text{CoCO}^+ + \text{M} \longrightarrow \text{CoM}^+ + \text{CO}$	(51%)
$\longrightarrow \text{CoC}_3\text{H}_4^+ + \text{HBr} + \text{CO}$	(43%)
$\longrightarrow \text{CoC}_3\text{H}_5^+ + \text{Br} + \text{CO}$	(6%)
$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow \text{CoM}^+ + 2\text{CO}$	(65%)
$\longrightarrow \text{CoCOM}^+ + \text{CO}$	(35%)
$\text{CoNO}^+ + \text{M} \longrightarrow \text{CoNOC}_3\text{H}_5^+ + \text{Br}$	(100%)
$\text{CoCONO}^+ + \text{M} \longrightarrow \text{CoNOM}^+ + \text{CO}$	(23%)
$\longrightarrow \text{CoCONOC}_3\text{H}_3^+ + \text{H}_2\text{Br}$	(77%)
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow \text{CoNOM}^+ + 2\text{CO}$	(80%)
$\longrightarrow \text{CoCONOM}^+ + \text{CO}$	(20%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow \text{CoNOM}^+ + 3\text{CO}$	(14%)
$\longrightarrow \text{CoCONOM}^+ + 2\text{CO}$	(53%)
$\longrightarrow \text{Co}(\text{CO})_2\text{NOM}^+ + \text{CO}$	(33%)

Table 19. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with
1-hydroxy-2-propene ($\text{M} = \text{CH}_2=\text{CHCH}_2\text{OH}$).

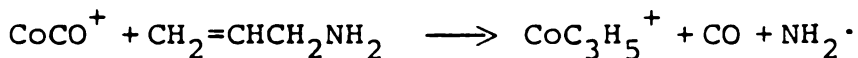
$\text{Co}^+ + \text{M} \longrightarrow$	$\text{CoC}_3\text{H}_4^+ + \text{H}_2\text{O}$	(100%)
$\text{CoCO}^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(93%)
	$\longrightarrow \text{CoC}_3\text{H}_4^+ + \text{H}_2\text{O} + \text{CO}$	(7%)
$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + 2\text{CO}$	(4%)
	$\longrightarrow \text{CoCOM}^+ + \text{CO}$	(96%)
$\text{CoNO}^+ + \text{M} \longrightarrow$	No Reaction	
$\text{CoCONO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(11%)
	$\longrightarrow \text{CoCONOM}^+ + \text{CO}$	(89%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 3\text{CO}$	(90%)
	$\longrightarrow \text{CoNOCOC}_3\text{H}_5^+ + \text{CO} + \text{COOH}$	(10%)

Table 20. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with allyl ether ($\text{M} = (\text{CH}_2=\text{CHCH}_2)_2\text{O}$).

$\text{Co}^+ + \text{M} \longrightarrow$	$\text{CoC}_3\text{H}_5^+ + \text{OC}_3\text{H}_5$	(100%)
$\text{CoCO}^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(12%)
	$\longrightarrow \text{CoCOC}_3\text{H}_5^+ + \text{OC}_3\text{H}_5$	(65%)
	$\longrightarrow \text{CoCOCH}_2\text{CHCHO}^+ + \text{C}_3\text{H}_6$	(23%)
$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + 2\text{CO}$	(78%)
	$\longrightarrow \text{CoCOCH}_2\text{CHCHO}^+ + \text{C}_3\text{H}_6 + \text{CO}$	(22%)
$\text{CoNO}^+ + \text{M} \longrightarrow$	No Reaction	
$\text{CoCONO}^+ + \text{M} \longrightarrow$	No Reaction	
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(60%)
	$\longrightarrow \text{CoNOC}_3\text{H}_5^+ + \text{C}_3\text{H}_5\text{O} + 2\text{CO}$	(16%)
	$\longrightarrow \text{CoCONOC}_3\text{H}_5^+ + \text{C}_3\text{H}_5\text{O} + \text{CO}$	(17%)
	$\longrightarrow \text{Co}(\text{CO})_2\text{NOC}_3\text{H}_5^+ + \text{C}_3\text{H}_5\text{O}$	(7%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 3\text{CO}$	(90%)
	$\longrightarrow \text{Co}(\text{CO})_2\text{NOC}_3\text{H}_5^+ + \text{C}_3\text{H}_5\text{O} + \text{CO}$	(10%)



Apparently Co^+ inserts readily into the allyl-X bonds because of the strong $\text{Co}^+-\text{C}_3\text{H}_5$ interaction. The formation of CoC_3H_5^+ from allyl amine places a lower limit on the bond strength: $D(\text{Co}^+-\text{C}_3\text{H}_5) > 69$ kcal/mole. The CoC_3H_5^+ formation reaction also occurs with allyl bromide, which implies $D(\text{Co}^+-\text{C}_3\text{H}_5) > 79$ kcal/mole. Since the following reaction also occurs

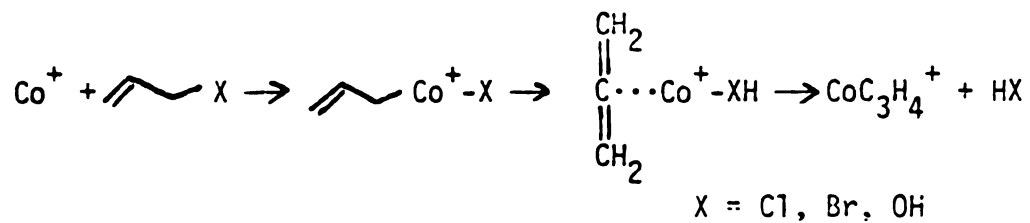


it follows that $D(\text{Co}^+-\text{C}_3\text{H}_5) > \{79 \text{ kcal/mole} + D(\text{Co}^+-\text{CO})\}$.

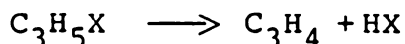
It has been suggested that the Co^+-NH_2 bond is very weak [7], which explains why CoNH_2^+ is not an observed reaction product. Thus, for the CoCO^+ ions, reactions with allyl amines are typical of amines. In addition, the fortuitous selection of the allyl group makes metal

insertion into this C-N bond thermodynamically accessible, and the products which follow such insertion are observed.

The chemistry of Co^+ is straightforward with allyl halides and alcohol. Apparently Co^+ eliminates HX from allyl chloride, bromide and alcohol by the mechanism previously discussed [47].

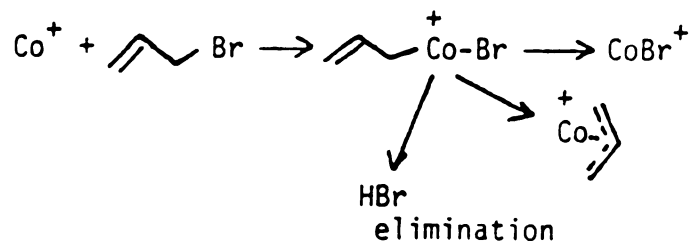


The energy required for the process



is fairly small and similar for these compounds, ranging from 19.9 kcal/mole for allyl alcohol to 25.1 for allyl bromide [43].

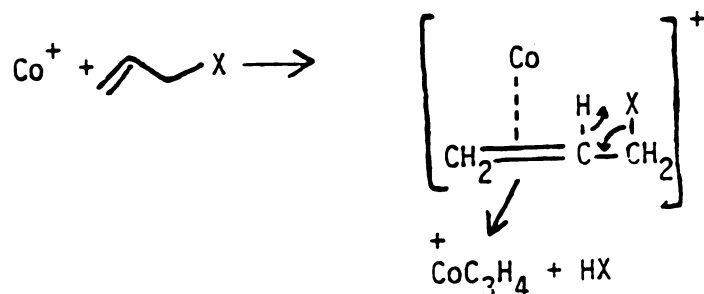
In the case of the bromide we see direct evidence for Co^+ insertion:



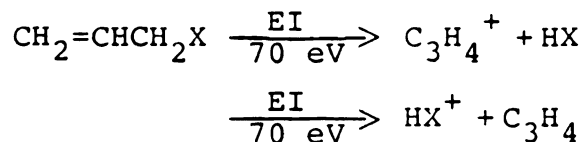
This may be evidence for $\text{D}(\text{Co}^+-\text{Br}) < \text{D}(\text{Co}^+-\text{Cl}) < \text{D}(\text{Co}^+-\text{OH})$. Note that in Table 18, CoNO^+ also reacts with allyl bromide by Br atom elimination. CoNO^+ was unreactive in all other

allylic compounds. This may be an indication of the weak cobalt ion-bromine atom bond.

When a metal ion reacts with allyl-X and HX elimination occurs one can take that as evidence for a metal insertion, β -H atom shift mechanism. Another possible explanation would be a dissociative attachment mechanism [3] in which the metal is not actively involved in the process — rather the complexation of the metal to the compound releases energy and the elimination occurs in the organic molecule, i.e.,

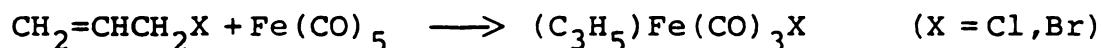


Evidence for the insertion, H shift mechanism has been reported for similar compounds [47]. As further evidence, the mass spectra of related compounds provide very useful information. Consider the halogenated compound-allyl bromide and allyl chloride. Both have fragment ions in their spectra which indicate HX elimination can occur for the compound alone.

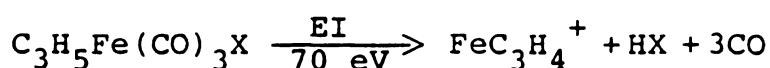


These ions are very minor in the mass spectra [48].

The mass spectra of metal-allyl halide compounds have also been reported. Iron complexes of this type, synthesized by the reaction [49]

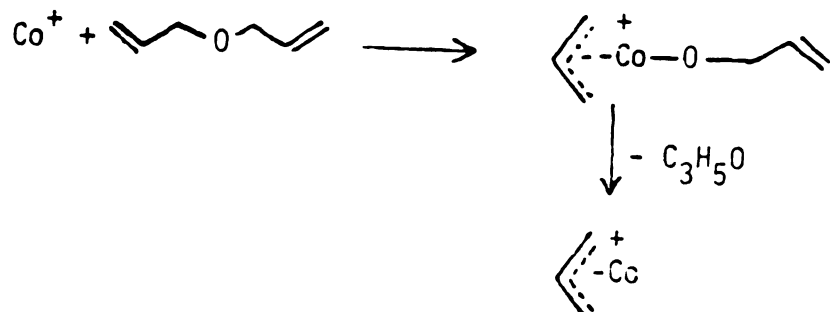


contain significant amounts of the elimination product [49],



Thus, with a metal present (and already inserted into the allyl-X bond), HX elimination becomes much more facile-supporting this mechanism.

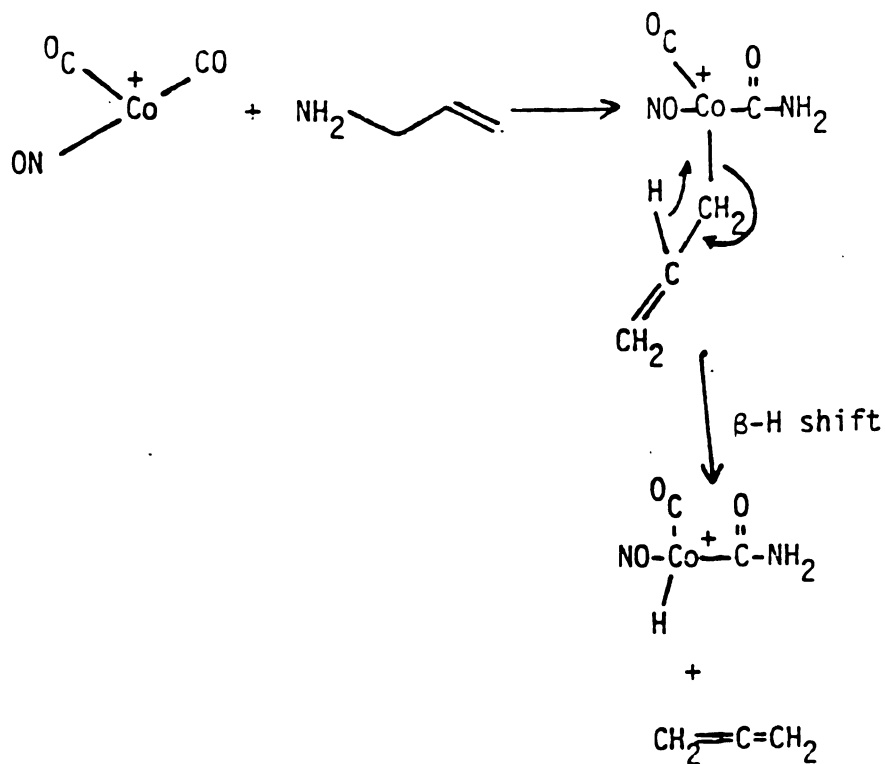
Allyl ether could be considered a trifunctional molecule or a bifunctional compound where the functional groups are a double bond and an -OR group. The presence of hydrogen atoms on the -OR functional group allows for additional mechanisms to occur. The metal center apparently inserts into the C-O bond of allyl ether; as implied by the CoC_3H_5^+ product.



This is not unexpected since allyl ether contains the weakest allyl-X bond of the compounds studied, $D(C_3H_5-OC_3H_5) = 66 \text{ kcal/mole}$ [43].

B. The Chemistry of CoL_n^+ Ions with Allyl Compounds.
Ligand Effects.

An interesting set of reactions are observed for the $Co(CO)_nNO^+$ ions with allyl amine. First, the reactivity of the $Co(CO)_nNO^+$ ions is the reverse of what is usually observed with monofunctional molecules. The lesser coordinated metal centers containing NO are less reactive. $CoNO^+$ and $CoCONO^+$ do not react, while the $Co(CO)_{2,3}NO^+$ do. Co^+ rearranges allyl amine into C_3H_4 and NH_3 , and eliminates NH_3 . $Co(CO)_2NO^+$ does the same, but retains the NH_3 . Since NH_3 retention requires the presence of CO's, and C_3H_4 can be eliminated without concurrent loss of the CO (in fact, at least one CO is always retained) CO may be involved in the reaction as follows:

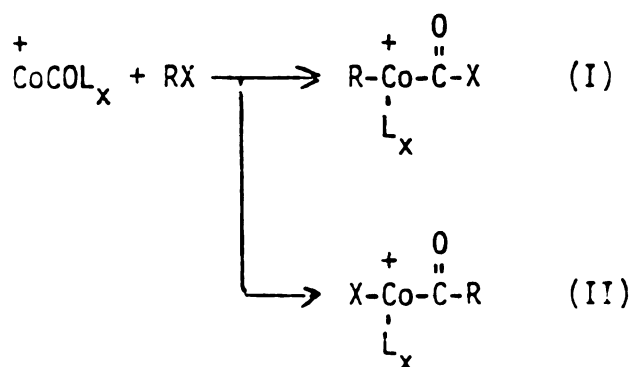


Here is proposed a CoCO^+ insertion into the C-N bond followed by a β -H atom shift. As the H atom shifts the cobalt remains tetra-coordinate. The allene, which cannot interact with the metal, is eliminated — leaving the elements of ammonia (as -NH_2 and -H) remaining in the complex.

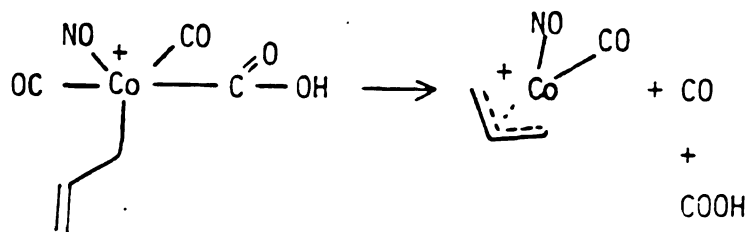
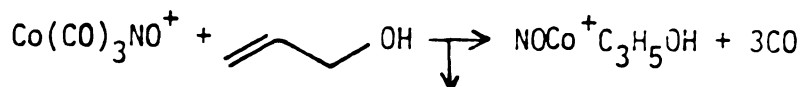
Allyl chloride, bromide and alcohol also participate in ligand substitution reactions — displacing one or more CO's as seen in Tables 17-19.

In the case of allyl alcohol (Table 19), again one sees the case of an increasing "reactivity" of the metal center as the number of ligands on the metal increases.

(By "reactivity", one is referring to processes other than simple ligand substitution.) For the $\text{Co}(\text{CO})_n\text{NO}^+$ ions, no reaction is observed for $n=0$, only ligand substitution is observed for $n=1$ and 2 , while substitution and OH loss is observed for $n=3$. Again this may evidence for insertion of CoCO into the C-OH bond. If a group of atoms such as CoCO inserts into RX , at least two possibilities exist:

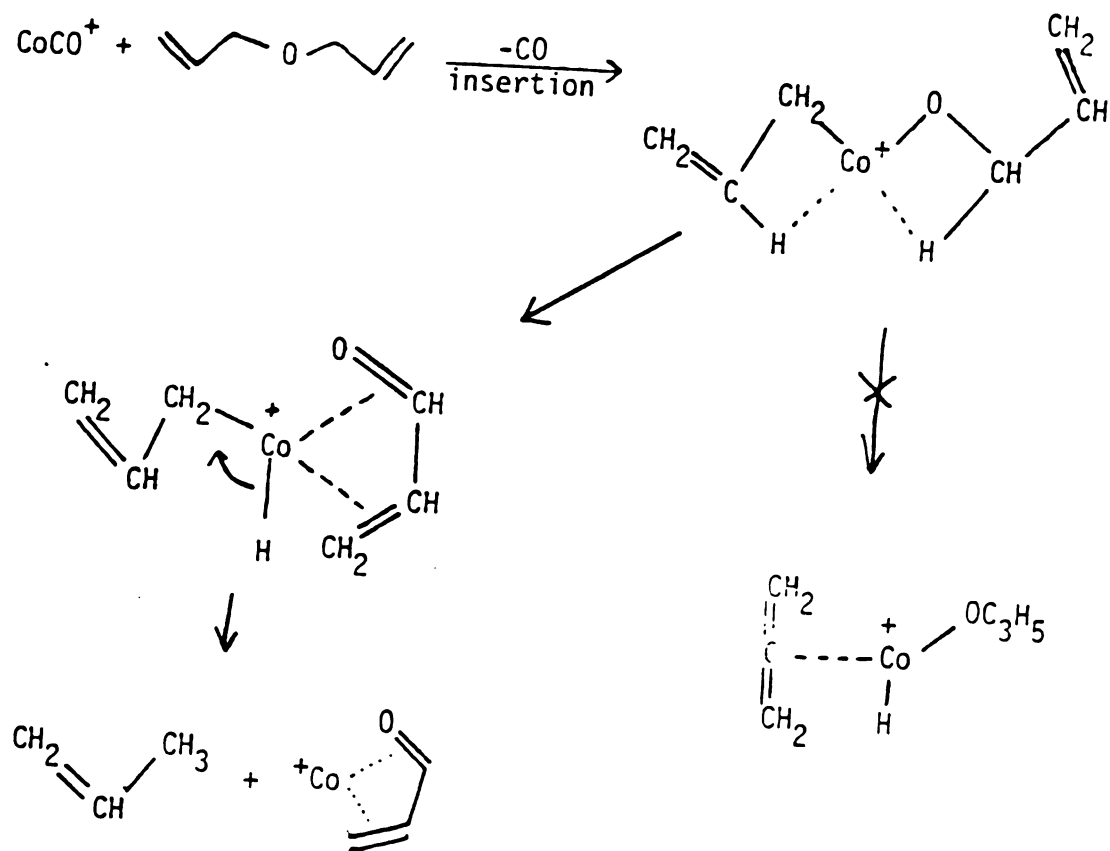


In the case of saturated compounds [7], the results have been explained by assuming that the alkyl group goes to the carbonyl, case (II) above. With allyl compounds, however, the strong allyl-metal interaction appears to direct the X-group to the carbonyl, case (I) above. Thus, the chemistry of $\text{Co}(\text{CO})_3\text{NO}^+$ with allyl alcohol is as follows:



As the CO and COOH are lost, the allyl group can change from a one electron donor to a three electron donor, as empty orbitals become available on the metal.

Following metal insertion, a β -H atom shift is common as a second mechanistic step, which in the other allyl compounds gave CoC_3H_4^+ as a product. In the case of allyl ether, the insertion product has two types of β -H atom. A shift of a β -H atom from the $-\text{OC}_3\text{H}_5$ group allows the complex to form a ligand similar to butadiene (i.e., propenal) which can efficiently donate four electrons to the electron deficient metal. This is seen in the reaction of CoCO^+ with allyl ether.



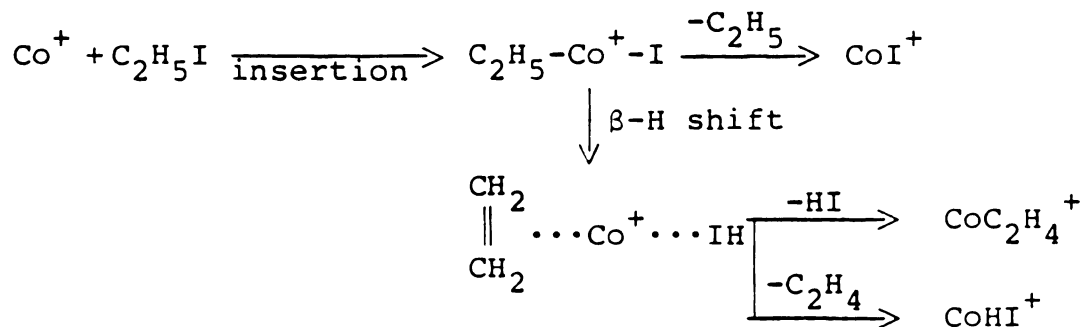
Note in Table 20, that the increasing reactivity of the $\text{Co}(\text{CO})_n\text{NO}^+$ ions with bifunctional molecules as n increases is also observed with allyl ether.

CHAPTER 7

THE CHEMISTRY OF COBALT-CONTAINING IONS WITH 2-CHLORO- AND 2-BROMOETHANOL

In Table 21 are the reactions for each metal ion with 2-chloroethanol along with the structure of the products. Also given are the branching ratios.

The chemistry of gas phase transition metal ions with alkyl halides has been reported [5,47]. For a number of alkyl halides, the recurring mechanism is a metal insertion, β -H atom shift sequence, from which all product ions can be explained [47]. For example, consider the reactions of Co^+ with ethyl iodide [47]:



The reaction of Co^+ with $\text{ClCH}_2\text{CH}_2\text{Br}$ would, then, be expected to yield HCl and/or Br elimination products to parallel metal-induced HI elimination from ethyl iodide.

Table 21. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with 2-chloroethanol ($\text{M} = \text{CH}_2\text{ClCH}_2\text{OH}$).

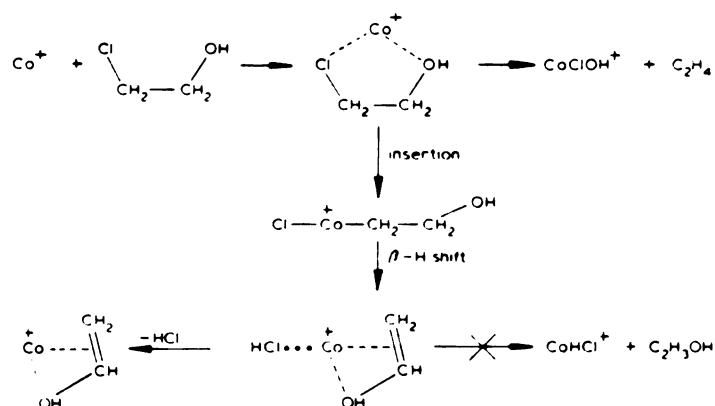
Co^+	$+ \text{M} \longrightarrow$	$\text{CoCH}_2\text{CHOH}^+ + \text{HCl}$	(44%)
	\longrightarrow	$\text{CoClOH}^+ + \text{CH}_2=\text{CH}_2$	(56%)
CoCO^+	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(10%)
		$\text{CoCOC1OH}^+ + \text{C}_2\text{H}_4$	
	\longrightarrow	$\text{CoCH}_2\text{CHOH}^+ + \text{HCl} + \text{CO}$	(52%)
	\longrightarrow	$\text{CoCOCH}_2\text{CHOH}^+ + \text{HCl}$	(7%)
	\longrightarrow	$\text{CoH}_2\text{O}^+ + \text{CH}_2\text{CHCl} + \text{CO}$	(22%)
	\longrightarrow	$\text{CoCOH}_2\text{O}^+ + \text{CH}_2\text{CHCl}$	(3%)
	\longrightarrow	$\text{CoCH}_2\text{OHCH}_2^+ + \text{Cl} + \text{CO}$	(4%)
	\longrightarrow	$\text{CoClOH}^+ + \text{C}_2\text{H}_4 + \text{CO}$	(2%)
$\text{Co}(\text{CO})_2^+$	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + 2\text{CO}$	(27%)
	\longrightarrow	$\text{CoCOM}^+ + \text{CO}$	(37%)
	\longrightarrow	$\text{CoCOCH}_2\text{CHOH}^+ + \text{HCl} + \text{CO}$	(9%)
	\longrightarrow	$\text{CoCOH}_2\text{O}^+ + \text{CH}_2\text{CHCl} + \text{CO}$	(22%)
	\longrightarrow	$\text{CoCOCH}_2\text{OHCH}_2^+ + \text{Cl} + \text{CO}$	(5%)
CoNO^+	$+ \text{M} \longrightarrow$	No Reaction	
CoCONO^+	$+ \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(35%)
	\longrightarrow	$\text{CoNOCH}_2\text{CHOH}^+ + \text{HCl} + \text{CO}$	(26%)
	\longrightarrow	$\text{CoNOH}_2\text{O}^+ + \text{CH}_2\text{ClCHCO}$	(25%)
	\longrightarrow	$\text{CoNOOH}^+ + \text{CH}_2\text{ClCHCO}$	(14%)

Table 21 Continues.

Table 21 Continued.

$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 2\text{CO}$	(54%)
	$\longrightarrow \text{CoCONOM}^+ + \text{CO}$	(5%)
	$\longrightarrow \text{CoNOCH}_2\text{CHOH}^+ + \text{HCl} + 2\text{CO}$	(9%)
	$\longrightarrow \text{CoCONOCH}_2\text{CHOH}^+ + \text{HCl} + \text{CO}$	(2%)
	$\longrightarrow \text{CoNOH}_2\text{O}^+ + \text{CH}_2\text{ClCHO} + \text{CO}$	(8%)
	$\longrightarrow \text{CoCONOH}_2\text{O}^+ + \text{CH}_2\text{ClCHCO}$	(9%)
	$\longrightarrow \text{CoNOOH}^+ + \text{CH}_2\text{ClCHCO} + \text{CO}$	(10%)
	$\longrightarrow \text{CoCONOOH}^+ + \text{CH}_2\text{ClCHCO}$	(3%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoCONOM}^+ + 2\text{CO}$	(48%)
	$\longrightarrow \text{CoCONOOH}^+ + \text{CH}_2\text{ClCH}_2\text{CO} + \text{CO}$	(20%)
	$\longrightarrow \text{CoCONOH}_2\text{O}^+ + \text{CH}_2\text{ClCHCO} + \text{CO}$	(15%)
	$\longrightarrow \text{CoCONOCH}_2\text{CHOH}^+ + \text{HCl} + 2\text{CO}$	(17%)

Apparently Co^+ interacts very strongly with both halogens and a cyclic intermediate is more stable than the metal-insertion type intermediate. Co^+ also forms products such as CoClOH^+ , with chloroethanol, indicative of a five membered ring intermediate. Co^+ also appears to insert into the C-Cl bond.



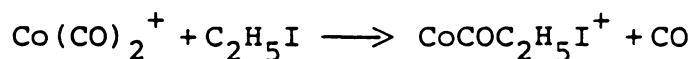
Following the β -H atom shift, the complex will lose HCl but not $\text{C}_2\text{H}_3\text{OH}$. This is an indication that the interaction of $\text{C}_2\text{H}_3\text{OH}$ with Co^+ is much stronger than if this species was simply ethene. Both the double bond and a lone pair on the oxygen can bond to the metal as shown. This also follows the proton affinity/metal affinities trends discussed in previous sections.

In terms of the analytical utility of metal ions as CI reagents in mass spectrometry, these results are intriguing. In the work done to date, specific mechanisms

are observed for specific functional groups. Alkyl chlorides react to give HCl elimination products. Alcohols react to give H₂O elimination products by an analogous mechanism [47]. The work of Freiser [39] indicates that when two functional groups are far removed in the molecule, products representative of both groups can be observed. Here investigation of neighboring functional groups were performed. In the case of 1-chloro-2-bromoethane the two groups react as a "new" group. Elimination of HX is not observed due to the strong halogen-metal interactions which restricts mechanistic access to HX elimination products. In the case of 2-chloroethanol, insertion and ring formation apparently compete as reaction intermediates. Thus in the case of adjacent functional groups it cannot be assumed that products indicative of each group will be observed in metal ion CI.

Another fascinating aspect of the chemistry of gas phase metallic species with bifunctional molecules is typified by the reactions in Table 21. Most of the current interest in this field today is the chemistry of the bare metal ions with organic molecules. Electron impact on metal-containing compounds generate metal centers with various numbers of ligands attached. In the case of metal carbonyls, as the number of CO's on the metal increases, the likelihood of any reaction except for ligand substitution decreases [5]. The previously reported reactions of the ions derived from Co(CO)₃NO with

ethyl iodide typify this behavior. Co^+ eliminates HI from ethyl iodide, as does CoCO^+ , but only ligand substitution is observed when 2 CO's are bound to the metal [5].

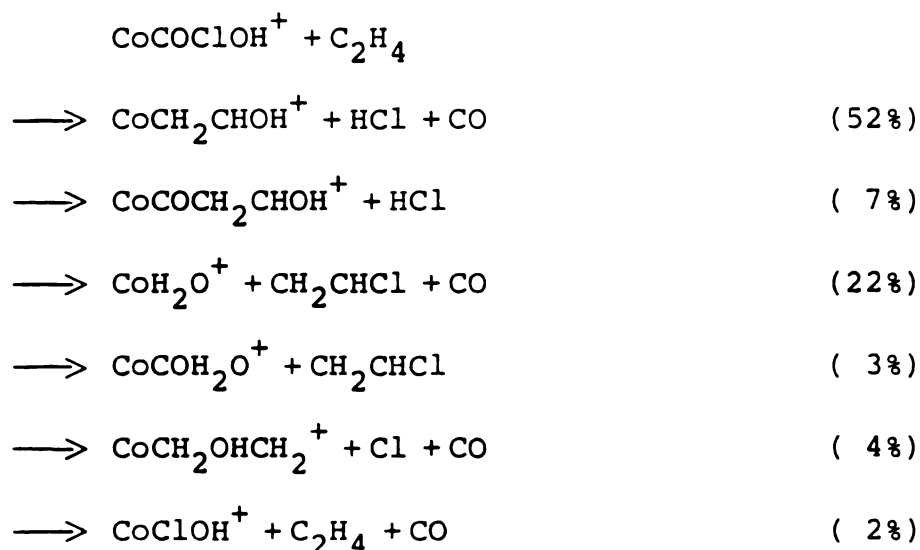


The same is observed for the $\text{Co}(\text{CO})_n\text{NO}^+$ ions. For $n=0$, the elimination reaction is observed, but for $n=1,2,3$ only displacement of 1 or 2 CO's by ethyl iodide is observed [5].

This is not the case for the compounds studied here.

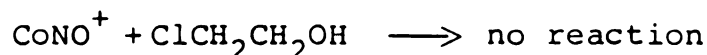
All of the metal containing ions derived from $\text{Co}(\text{CO})_3\text{NO}$ exhibit a rich chemistry with bifunctional molecules. Presumably, in cases where two groups can bond to the metal, much more energy is released in the intermediate complex than in the case of monofunctional molecules. In general, the chemistry observed in these mixtures is much richer and more varied than mixtures involving monofunctional molecules.

A number of interesting changes occur in the chemistry of a metal ion as ligands are added to the metal. Co^+ alone reacts with 2-chloroethanol by oxidative addition to form CoClOH- , and by HCl elimination. CoCO^+ appears to react by metal insertion into the C-Cl or the C-OH bonds and also by a cyclic intermediate.

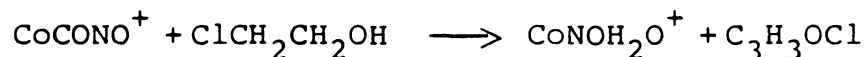


There are also a number of processes in which the ligands may become more than just spectators in a reaction, but may be ultimately involved in the overall process.

To give one of a number of this type of reactions which can be found in Table 21, consider the following: CoNO^+ does not react with 2-chloroethanol.

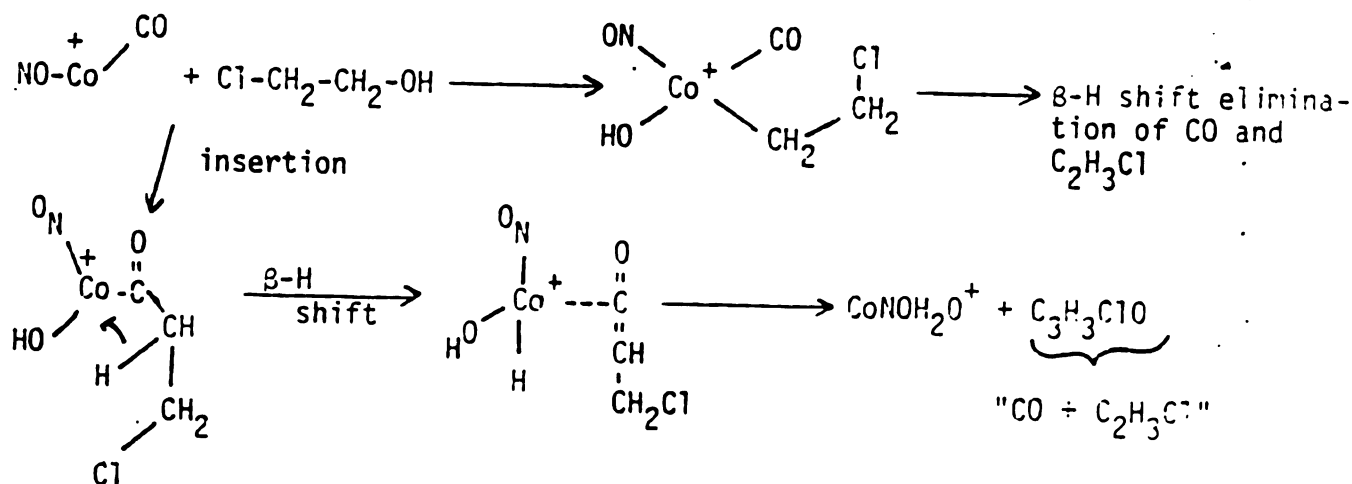


With one CO present, H_2O elimination is observed.



If the 2-chloroethanol rearranged to H_2O and vinyl chloride on the metal, H_2O elimination and vinyl chloride retention would be expected due to the possibility of multiple

ligand-metal interactions with vinyl chloride. This is not observed. Since the reaction is only observed with concurrent CO elimination, this may be evidence for, not Co^+ insertion, but CoCO^+ insertion into a polar bond, i.e.,



1. 2-Bromoethanol

In Table 22 is a summary of the reactions for each of the metal containing ions with this compound as well as the branching ratios.

The chemistry of Co^+ with 2-bromoethanol is richer than with 2-chloroethanol. The analogous reactions for the Co^+ ion are present in 2-bromoethanol but to a lesser extent due to other reactions being observed. A five member intermediate is again proposed for the elimination of C_2H_4 . However the elimination of BrOH also occurs. From the identical branching ratios, these two ligands

Table 22. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with 2-bromoethanol ($\text{M} = \text{CH}_2\text{BrCH}_2\text{OH}$).

$\text{Co}^+ + \text{M} \longrightarrow$	$\text{CoCH}_2\text{CHOH}^+ + \text{HBr}$	(3%)
\longrightarrow	$\text{CoBrOH}^+ + \text{CH}_2=\text{CH}_2$	(15%)
\longrightarrow	$\text{CoCH}_2\text{CH}_2\text{OH}^+ + \text{Br}$	(4%)
\longrightarrow	$\text{CoC}_2\text{H}_4^+ + \text{BrOH}$	(15%)
\longrightarrow	$\text{CH}_2\text{CH}_2\text{Br}^+ + \text{CoOH}$	(25%)
\longrightarrow	$\text{CoOH}^+ + \text{CH}_2\text{CH}_2\text{Br}$	(8%)
\longrightarrow	$\text{CoCH}_2\text{CH}_2\text{Br}^+ + \text{OH}$	(13%)
\longrightarrow	$\text{CoCH}_2\text{Br}^+ + \text{CH}_2\text{OH}$	(7%)
\longrightarrow	$\text{Co}(\text{M-H})^+ + \text{H}$	(5%)
$\text{CoCO}^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(5%)
	$\text{CoCOBrOH}^+ + \text{C}_2\text{H}_4$	
\longrightarrow	$\text{CoCH}_2\text{CHOH}^+ + \text{HBr} + \text{CO}$	(34%)
\longrightarrow	$\text{CoH}_2\text{O}^+ + \text{CH}_2\text{CHBr} + \text{CO}$	(12%)
\longrightarrow	$\text{CoCOH}_2\text{O}^+ + \text{CH}_2\text{CHBr}$	(6%)
\longrightarrow	$\text{CoCH}_2\text{OHCH}_2^+ + \text{Br} + \text{CO}$	(6%)
	$\text{CoCOOH}^+ + \text{CH}_2\text{CH}_2\text{Br}$	
\longrightarrow	$\text{CoBrOH}^+ + \text{C}_2\text{H}_4 + \text{CO}$	(2%)
\longrightarrow	$\text{CoCOC}_2\text{H}_4^+ + \text{BrOH}$	(9%)
\longrightarrow	$\text{CH}_2\text{BrCH}_2^+ + \text{CoCOOH}$	(14%)
\longrightarrow	$\text{CoCH}_2\text{BrCH}_2^+ + \text{CO} + \text{OH}$	(6%)
\longrightarrow	$\text{CoCH}_2\text{Br}^+ + \text{CH}_2\text{OH} + \text{CO}$	(3%)
\longrightarrow	$\text{Co}(\text{M-H})^+ + \text{H} + \text{CO}$	(3%)

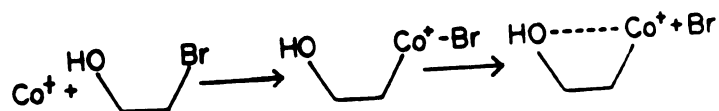
Table 22 Continues.

Table 22 Continued.

$\text{Co}(\text{CO})_2^+ + \text{M} \longrightarrow$	$\text{CoCOM}^+ + \text{CO}$	(78%)
\longrightarrow	$\text{CoCOH}_2\text{O}^+ + \text{CH}_2\text{CHBr} + \text{CO}$	(22%)
$\text{CoNO}^+ + \text{M} \longrightarrow$	No Reaction	
$\text{CoCONO}^+ + \text{M} \longrightarrow$	No Reaction	
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(82%)
\longrightarrow	$\text{CoNOHCOOH}^+ + \text{CH}_2\text{BrCH}=\text{C}=\text{O}$	(8%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 3\text{CO}$	(15%)
\longrightarrow	$\text{CoCONOM}^+ + 2\text{CO}$	(70%)
\longrightarrow	$\text{CoNOHCOOH}^+ + \text{CH}_2\text{BrCH}=\text{C}=\text{O} + \text{CO}$	(5%)
\longrightarrow	$\text{CoCONOHCOOH}^+ + \text{CH}_2\text{BrCHCO}$	(10%)

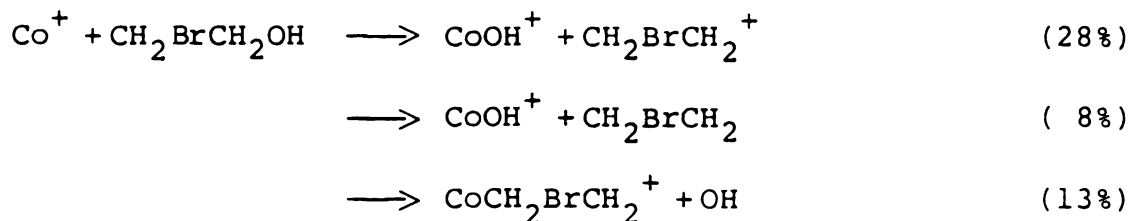
are retained by Co^+ to the same extent. This may be due to similar metal-ligand affinities.

As was observed in allyl bromide, we see direct evidence for Co^+ insertion:



Small amounts of Br atom elimination were observed (4%). This again is evidence for $D(\text{Co}^+-\text{Br}) < D(\text{Co}^+-\text{Cl})$.

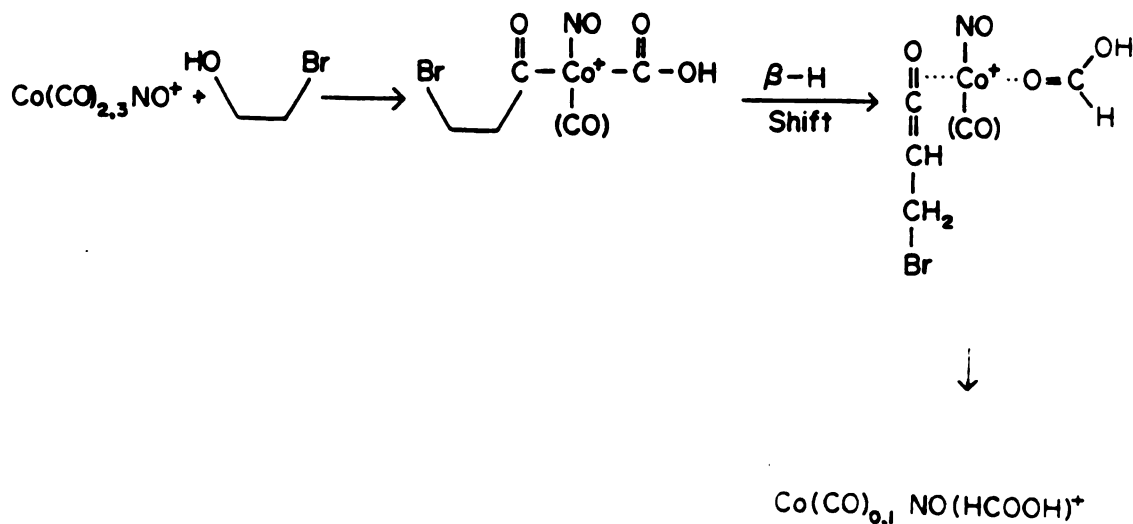
In 2-chloroethanol, attack at C-OH was not observed for the Co^+ ion. However in 2-bromoethanol 49% of the total reactions of this ion occur at this site. In each of the three reactions at this site radicals are formed.



CoCO^+ reacts just as Co^+ does with 2-bromoethanol. In most cases, the CO is also lost in the reaction. Just as it was in 2-chloroethanol, CoCO^+ forms CoCOH_2O^+ and CoH_2O^+ in this mixture while Co^+ does not. This is a new

reaction that occurs for these ions and is not due to the ligand participation reaction since the CO is both lost and retained by the metal ion.

The chemistry of $\text{Co}(\text{CO})_2\text{NO}^+$ and $\text{Co}(\text{CO})_3\text{NO}^+$ are dominated by ligand substitution reactions (92% and 85%, respectively). The remaining chemistry of these ions involves insertion of CoCO^+ into the C-OH bond with a CO inserting onto both fractions of 2-bromoethanol, followed by a β -H atom shift and the elimination $\text{CH}_2\text{BrCH}=\text{C}=\text{O}$ from the intermediate $(\text{CH}_2\text{BrCHCO})\text{Co}^+(\text{CO})_n\text{NO}(\text{HCOOH})$ ($n = 0$ for $\text{Co}(\text{CO})_2\text{NO}^+$ and $n = 0, 1$ for $\text{Co}(\text{CO})_3\text{NO}^+$).



Since these reactions do not occur for CoNO^+ and CoCONO^+ , further evidence for two CO's insertion is provided.

CHAPTER 8

THE CHEMISTRY OF COBALT-CONTAINING IONS WITH SUBSTITUTED BUTANONES

As stated earlier, most compounds which are subject to analysis today by mass spectrometry are multifunctional in nature. Using chemical ionization, it is useful to have knowledge of any preference a reagent ion has for different functional groups in order to evaluate a CI spectrum of an unknown. In the continuing efforts to investigate whether metal ions can be utilized as CI reagents, bifunctional ketones and carboxylic acids were studied.

In this discussion, using what has been established as reaction pathways for the various functional groups involved, we have been able to predict products based upon the assumption that products representative of each functional group will be formed. When a metal insertion/ β -H shift leads to the intermediate of the type $\text{Co}^+(\text{A})(\text{B})$, where further decomposition of, e.g., B, have been observed, these reactions were also predicted. The predicted reactions with the branching ratios for those observed are given in Table 23.

TABLE 23 Reactions Predicted For Co^+ with 3- Substituted Butanones

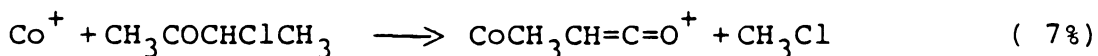
Reactions Predicted For Ketone Functional Group		% Observed		
		X=Cl	X=Br	X=OH
$\text{Co}^+ + \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{CH}_2-\text{X} \end{array} \rightarrow \begin{array}{l} \xrightarrow{\text{A}} (\text{CH}_3)_2\text{Co}^+(\text{CO})(\text{C}_2\text{H}_5\text{X}) \xrightarrow{\quad} \text{Co}(\text{CO})(\text{C}_2\text{H}_5\text{X})^+ + \text{CH}_4 \\ \xrightarrow{\text{B}} (\text{CH}_3\text{CHO})\text{Co}^+(\text{C}_2\text{H}_5\text{X}) \xrightarrow{\quad} \text{CoC}_2\text{H}_5\text{X}^+ + \text{CH}_3\text{CHO} \\ \xrightarrow{\quad} \text{CoCH}_3\text{CHO}^+ + \text{C}_2\text{H}_5\text{X} \end{array}$		9		3
		5		12
Reactions Predicted For X- Functional Group				
$\text{Co}^+ + \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{CH}_2-\text{X} \end{array} \rightarrow \begin{array}{l} \xrightarrow{\quad} \text{CoX} + \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{CH}_2\cdot \end{array} \\ \xrightarrow{\quad} \text{Co}(\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{CH}_2\cdot \end{array})^+ + \text{X}\cdot \\ \xrightarrow[\text{Shift}]{\text{A-H}} (\text{HX})\text{Co}^+(\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{CH}_2\cdot \end{array}) \xrightarrow{\quad} \text{CoHX}^+ + \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{CH}_2\cdot \end{array} \\ \xrightarrow{\quad} \text{Co}(\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{CH}_2\cdot \end{array})^+ + \text{HX} \end{array}$		6	15	4
				3
		35	55	32
Predicted Subsequent Reactions of Intermediate D				
$(\text{HX})\text{Co}^+(\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{CH}_2\cdot \end{array}) \rightarrow \begin{array}{l} \xrightarrow{\quad} (\text{HX})\text{Co}^+(\text{CO})(\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{CH}_2\cdot \end{array}) \xrightarrow{\quad} \text{CoC}_3\text{H}_6^+ + \text{CO} + \text{HX} \\ \xrightarrow{\quad} \text{CoCO}^+ + \text{C}_3\text{H}_6 + \text{HX} \\ \xrightarrow{\quad} (\text{HX})\text{Co}^+(\text{C}_2\text{H}_5)(\text{CH}_3\text{CHO})^+ \rightarrow \text{COC}_2\text{H}_5^+ + \text{HX} + \text{CH}_3\text{CHO} \\ \xrightarrow{\quad} (\text{HX})\text{Co}^+(\text{C}_2\text{H}_5)(\text{CH}_3)(\text{CO}) \rightarrow \text{Co}(\text{CO})(\text{C}_2\text{H}_5)^+ + \text{HX} + \text{CH}_4 \end{array}$		18	30	13
		9		11
		5		
		6		
Total of Reaction Products Predicted		93%	100%	78%

The discussion of the chemistry of CoL_n^+ ions will follow the approach used with other mixtures. Ligand substitution reactions will be noted as well as similar chemistry of the CoL_n^+ to Co^+ but the emphasis will be on new reactions involving ligand participation.

A. The Chemistry of Co^+ with 3-Substituted Butanones

In Tables 24-26 are the reactions of each metal ion with 3-X-butanone ($\text{X} = \text{Cl}, \text{Br}, \text{OH}$), respectively, along with the branching ratios.

In 3-chlorobutanone, 93% of the reactions were predicted (see Table 23). The only observed reaction that was not predicted was the elimination of CH_3Cl . Apparently, following metal insertion into the C-Cl bond, a β -H or β -methyl shift can occur leading to HCl and CH_3Cl elimination.



Assuming that the last set of reactions in Table 27 are due from further decomposition of the intermediate $\text{Co}(\text{HCl})(\text{CH}_3\text{COCH}=\text{CH}_2)^+$, 86% of the reactions of 3-chlorobutanone are due to initial attack at the chlorine by Co^+ .

Two of the possible products in the substituted butanones (products from intermediate C) are suggested by

Table 24. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with
3-chlorobutanone ($\text{M} = \text{CH}_3\text{COCHClCH}_3$).

Co^+	$+ \text{M} \longrightarrow$	$\text{CoCO}(\text{C}_2\text{H}_3\text{Cl})^+ + \text{CH}_4$	(9%)
		$\text{CoCH}_3\text{CCl}=\text{C}=\text{O}^+ + \text{CH}_4$	
	\longrightarrow	$\text{CoCH}_3\text{CHO}^+ + \text{C}_2\text{H}_3\text{Cl}$	(5%)
	\longrightarrow	$\text{CoCH}_3\text{COCH}=\text{CH}_2^+ + \text{HCl}$	(35%)
	\longrightarrow	$\text{CoCO}^+ + \text{HCl} + \text{C}_3\text{H}_6$	(9%)
	\longrightarrow	$\text{CoC}_3\text{H}_6^+ + \text{HCl} + \text{CO}$	(18%)
	\longrightarrow	$\text{CoCH}_3\text{CH}=\text{C}=\text{O}^+ + \text{CH}_3\text{Cl}$	(7%)
	\longrightarrow	$\text{CoCH}_3\text{COCHCH}_3^+ + \text{Cl}$	(6%)
	\longrightarrow	$\text{CoCOC}_2\text{H}_2^+ + \text{CH}_4 + \text{HCl}$	(6%)
	\longrightarrow	$\text{CoC}_2\text{H}_2^+ + \text{HCl} + \text{CH}_3\text{CHO}$	(5%)
CoCO^+	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(3%)
	\longrightarrow	$\text{CoCOCH}_3\text{COCH}=\text{CH}_2^+ + \text{HCl}$	(10%)
	\longrightarrow	$\text{CoCH}_3\text{COCH}=\text{CH}_2^+ + \text{HCl} + \text{CO}$	(66%)
	\longrightarrow	$\text{CoCH}_3\text{COCHCH}_3^+ + \text{Cl} + \text{CO}$	(5%)
	\longrightarrow	$\text{CoCOCH}_3\text{CHO}^+ + \text{C}_2\text{H}_3\text{Cl} \quad /$	(7%)
		$\text{CoCOCH}_3\text{CHO}^+ + \text{C}_2\text{H}_2 + \text{HCl}$	
	\longrightarrow	$\text{CoCH}_3\text{CH}=\text{C}=\text{O}^+ + \text{CH}_3\text{Cl} + \text{CO}$	(9%)
$\text{Co}(\text{CO})_2^+$	$+ \text{M} \longrightarrow$	$\text{CoM}^+ + 2\text{CO}$	(52%)
	\longrightarrow	$\text{CoCOM}^+ + \text{CO}$	(31%)
	\longrightarrow	$\text{CoCH}_3\text{COCH}=\text{CH}_2^+ + \text{HCl} + 2\text{CO}$	(17%)
CoNO^+	$+ \text{M} \longrightarrow$	No Reaction	

Table 24 Continues.

Table 24 Continued.

$\text{CoCONO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + \text{CO}$	(42%)
	$\longrightarrow \text{CoNOCH}_3\text{COCH=CH}_2^+ + \text{HCl} + \text{CO}$	(58%)
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 2\text{CO}$	(97%)
	$\longrightarrow \text{CoNOCH}_3\text{COCH=CH}_2^+ + \text{HCl} + 2\text{CO}$	(3%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 3\text{CO}$	(51%)
	$\longrightarrow \text{CoCONOM}^+ + 2\text{CO}$	(49%)

Table 25. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with 3-bromobutanone ($\text{M} = \text{CH}_3\text{COCHBrCH}_3$).

<hr/>		
Co^+	$+ \text{M} \longrightarrow \text{CoCH}_3\text{COCH}=\text{CH}_2^+ + \text{HBr}$	(55%)
	$\longrightarrow \text{CoC}_3\text{H}_6^+ + \text{HBr} + \text{CO}$	(30%)
	$\longrightarrow \text{CoCH}_3\text{COCHCH}_3^+ + \text{Br}$	(15%)
CoCO^+	$+ \text{M} \longrightarrow \text{CoM}^+ + \text{CO}$	*
	$\longrightarrow \text{CoC}_2\text{H}_3\text{Br}^+ + \text{CH}_3\text{CHO}$	(8%)
	$\text{CoC}_2\text{H}_3\text{Br}^+ + \text{CH}_4 + \text{CO}$	
	$\longrightarrow \text{CoCOCH}_3\text{COCH}=\text{CH}_2^+ + \text{HBr}$	(7%)
	$\longrightarrow \text{CoCH}_3\text{COCH}=\text{CH}_2^+ + \text{HBr} + \text{CO}$	(74%)
	$\longrightarrow \text{CoCH}_3\text{COCHCH}_3^+ + \text{Br} + \text{CO}$	(5%)
	$\longrightarrow \text{CoCH}_3\text{CHO}^+ + \text{C}_2\text{H}_3\text{Br}$	(6%)
$\text{Co}(\text{CO})_2^+$	$+ \text{M} \longrightarrow \text{CoM}^+ + 2\text{CO}$	*
	$\longrightarrow \text{CoCOM}^+ + \text{CO}$	*
	$\longrightarrow \text{CoCOCH}_3\text{COCH}=\text{CH}_2^+ + \text{HBr} + \text{CO}$	(26%)
	$\longrightarrow \text{CoCOC}_2\text{H}_3\text{Br}^+ + \text{CH}_3\text{CHO} + \text{CO}$	(74%)
	$\text{CoCOC}_2\text{H}_3\text{Br}^+ + \text{CH}_4 + 2\text{CO}$	
CoNO^+	$+ \text{M} \longrightarrow \text{CoNOCH}_3\text{COCHCH}_3^+ + \text{Br}$	(100%)
CoCONO^+	$+ \text{M} \longrightarrow \text{CoNO}(\text{M}-\text{HBr})^+ + \text{HBr} + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+$	$+ \text{M} \longrightarrow \text{CoNOM}^+ + 2\text{CO}$	*
	$\longrightarrow \text{CoCONOM}^+ + \text{CO}$	*
<hr/>		

Table 25 Continues.

Table 25 Continued.

$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 3\text{CO}$	*
	$\longrightarrow \text{CoCONOM}^+ + 2\text{CO}$	*
	$\longrightarrow \text{Co}(\text{CO})_2\text{NOM}^+ + \text{CO}$	*
	$\longrightarrow \text{CoCONO}(\text{M-HBr})^+ + \text{HBr} + \text{CO}$	(27%)
	$\longrightarrow \text{Co}(\text{CO})_2\text{NO}(\text{M-HBr})^+ + \text{HBr} + \text{CO}$	(13%)
	$\longrightarrow \text{CoNOC}_2\text{HBr}^+ + \text{CH}_3\text{CHO} + 3\text{CO}$	(60%)

* Peaks at m/z corresponding to these ions were of too low an intensity to perform double resonance.

Table 26. Reactions of the ions of $\text{Co}(\text{CO})_3\text{NO}$ with 3-hydroxybutanone ($\text{M} = \text{CH}_3\text{COCHOHCH}_3$).

$\text{Co}^+ + \text{M} \longrightarrow$	$\text{CoCOC}_2\text{H}_3\text{OH}^+ + \text{CH}_4$ $\text{CoCH}_3\text{COH}=\text{C}=\text{O}^+ + \text{CH}_4$	(3%)
\longrightarrow	$\text{CoCH}_3\text{CHO}^+ + \text{C}_2\text{H}_3\text{OH}$ $\text{CoCH}_2=\text{CHOH}^+ + \text{CH}_3\text{CHO}$	(12%)
\longrightarrow	$\text{CoCH}_3\text{COCH}=\text{CH}_2^+ + \text{H}_2\text{O}$	(32%)
\longrightarrow	$\text{CoCO}^+ + \text{H}_2\text{O} + \text{C}_3\text{H}_6$	(11%)
\longrightarrow	$\text{CoC}_3\text{H}_6^+ + \text{CO} + \text{H}_2\text{O}$	(13%)
\longrightarrow	$\text{CoCH}_3\text{CH}=\text{C}=\text{O}^+ + \text{CH}_3\text{OH}$	(2%)
\longrightarrow	$\text{CoCH}_3\text{COCHCH}_3^+ + \text{OH}$	(4%)
\longrightarrow	$\text{CoH}_2\text{O}^+ + \text{CH}_3\text{COCH}=\text{CH}_2$	(3%)
\longrightarrow	$\text{CoCHOHCH}_3^+ + \text{CH}_3\text{CO}$	(4%)
\longrightarrow	$\text{CoCOCHOHCH}_3^+ + \text{CH}_3$	(3%)
\longrightarrow	$\text{CoCH}_3\text{COCOHCH}_3^+ + \text{H}$	(13%)
$\text{CoCO}^+ + \text{M} \longrightarrow$	$\text{CoM}^+ + \text{CO}$	(17%)
\longrightarrow	$\text{CoH}_2\text{O}^+ + \text{CH}_3\text{COCH}=\text{CH}_2 + \text{CO}$	(5%)
\longrightarrow	$\text{CoCOCH}_3\text{COCH}=\text{CH}_2^+ + \text{H}_2\text{O}$	(2%)
\longrightarrow	$\text{CoCH}_2=\text{CHOH}^+ + \text{CH}_3\text{CHO} + \text{CO} /$ $\text{CoCH}_3\text{CHO}^+ + \text{C}_2\text{H}_3\text{OH} + \text{CO}$	(4%)
\longrightarrow	$\text{Co}(\text{CO})\text{C}_2\text{H}_3\text{OH}^+ + \text{CH}_4 + \text{CO} /$ $\text{Co}(\text{CO})\text{CH}_3\text{CHO}^+ + \text{C}_2\text{H}_3\text{OH} /$ $\text{Co}(\text{CO})\text{C}_2\text{H}_3\text{OH}^+ + \text{CH}_3\text{CHO} /$ $\text{CoCH}_3\text{COH}=\text{C}=\text{O}^+ + \text{CH}_4 + \text{CO}$	(9%)
\longrightarrow	$\text{CoCOCHOHCH}_3^+ + \text{CH}_3\text{CO}$	(10%)
\longrightarrow	$\text{CoCOCH}_3\text{COCH}=\text{CH}_2^+ + \text{H}_2\text{O} + \text{CO}$	(34%)

Table 26 Continues.

Table 26 Continued.

————>	$\text{CoCH}_3\text{COCHCH}_3^+ + \text{OH} + \text{CO}$	(3%)
————>	$\text{CoCO}(\text{CO})\text{CH}_2\text{CHOH}^+ + \text{CH}_4$	(16%)
$\text{Co}(\text{CO})_2^+ + \text{M}$ ———>	$\text{CoM}^+ + 2\text{CO}$	(1%)
————>	$\text{CoCOM}^+ + \text{CO}$	(22%)
————>	$\text{CoCOH}_2\text{O} + \text{CH}_3\text{COCH}=\text{CH}_2 + \text{CO}$	(10%)
————>	$\text{CoCOCH}_2\text{CHOH}^+ + \text{CH}_4 + 2\text{CO} /$ $\text{CoCOCH}_3\text{CHO}^+ + \text{CH}_2\text{CHOH} + \text{CO} /$ $\text{CoCOCH}_2\text{CHOH}^+ + \text{CH}_3\text{CHO} + \text{CO} /$ $\text{CoCH}_3\text{COH}=\text{C}=\text{O}^+ + \text{CH}_4 + 2\text{CO}$	(6%)
————>	$\text{CoCO}(\text{CO})\text{CH}_2\text{CHOH}^+ + \text{CH}_4 + \text{CO} /$ $\text{Co}(\text{CO})_2\text{CH}_3\text{CHO}^+ + \text{CH}_2\text{CHOH}^+ /$ $\text{Co}(\text{CO})_2\text{CH}_2\text{CHOH}^+ + \text{CH}_3\text{CHO} /$ $\text{Co}(\text{CO})\text{CH}_3\text{COH}=\text{C}=\text{O}^+ + \text{CH}_4 + \text{CO}$	(44%)
————>	$\text{Co}(\text{CO})\text{COCHOHCH}_3^+ + \text{CH}_3 + \text{CO} /$ $\text{Co}(\text{CO})_2\text{CHOHCH}_3^+ + \text{CH}_3\text{CO}$	(18%)
$\text{CoNO}^+ + \text{M}$ ———>	No Reaction	
$\text{CoCONO}^+ + \text{M}$ ———>	$\text{CoNOM}^+ + \text{CO}$	(5%)
————>	$\text{CoCHOHCH}_3^+ + \text{CH}_3\text{CO} + \text{CO}$	(18%)
————>	$\text{CoNO}(\text{CO})\text{C}_2\text{H}_3\text{OH}^+ + \text{CH}_4 + \text{CO} /$ $\text{CoCONOCH}_3\text{CHO}^+ + \text{CH}_2\text{CHOH} /$ $\text{CoCONOC}_2\text{H}_3\text{OH}^+ + \text{CH}_3\text{CHO} /$ $\text{CoNOCH}_3\text{COH}=\text{C}=\text{O}^+ + \text{CH}_4 + \text{CO}$	(71%)
————>	$\text{CoCONOCHOHCH}_3^+ + \text{CH}_3\text{CO}$	(6%)

Table 26 Continues

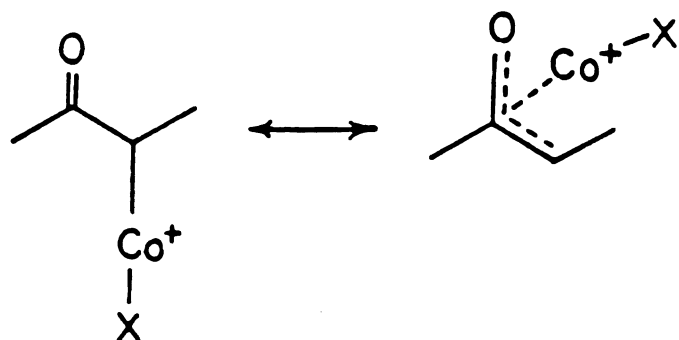
Table 26 Continued.

$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(43%)
\longrightarrow	$\text{CoNOH}_2\text{O}^+ + \text{CH}_3\text{COCH}=\text{CH}_2 + 2\text{CO}$	(3%)
\longrightarrow	$\text{CoCONOH}_2\text{O}^+ + \text{CH}_3\text{COCH}=\text{CH}_2 + \text{CO}$	(2%)
\longrightarrow	$\text{Co}(\text{CO})_2\text{NOH}_2\text{O}^+ + \text{M}-\text{H}_2\text{O} + \text{CO}$	(1%)
\longrightarrow	$\text{CoNO}(\text{CO})\text{C}_2\text{H}_3\text{OH}^+ + \text{CH}_4 + 2\text{CO}/$ $\text{CoCONOC}_2\text{H}_3\text{OH}^+ + \text{CH}_3\text{CHO} + \text{CO}/$ $\text{CoCONOCH}_3\text{CHO}^+ + \text{C}_2\text{H}_3\text{OH} + \text{CO}/$ $\text{CoNOCH}_3\text{COH}=\text{C}=\text{O}^+ + \text{CH}_4 + 2\text{CO}$	(38%)
\longrightarrow	$\text{CoCONOCHOHCH}_3^+ + \text{CH}_3\text{CO} + \text{CO}$	(13%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 3\text{CO}$	(58%)
\longrightarrow	$\text{CoCONOH}_2\text{O}^+ + \text{M}-\text{H}_2\text{O} + 2\text{CO}$	(1%)
\longrightarrow	$\text{Co}(\text{CO})_2\text{NOH}_2\text{O}^+ + \text{M}-\text{H}_2\text{O} + \text{CO}$	(2%)
\longrightarrow	$\text{CoCONO}(\text{CO})\text{C}_2\text{H}_3\text{OH} + \text{CH}_4 + 2\text{CO} /$ $\text{Co}(\text{CO})_2\text{NOCH}_3\text{CHO}^+ + \text{C}_2\text{H}_3\text{OH} + \text{CO}/$ $\text{Co}(\text{CO})_2\text{NOC}_2\text{H}_3\text{OH}^+ + \text{CH}_3\text{CHO} + \text{CO}/$ $\text{CoNOCH}_3\text{COH}=\text{C}=\text{O}^+ + \text{CH}_4 + 2\text{CO}$	(23%)
\longrightarrow	$\text{Co}(\text{CO})_2\text{NOCHOHCH}_3^+ + \text{CH}_3\text{CO} + \text{CO}$	(10%)

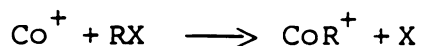
TABLE 27 Reactions Predicted For Co⁺ with 3- Substituted Butanones

Reactions Predicted For Ketone Functional Group		% Observed		
		X=Cl	X=Br	X=OH
$\text{Co}^+ + \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}(\text{CH}_3)\text{CH}_2\text{X} \end{array} \rightarrow \begin{array}{l} \text{A} \\ \text{B} \end{array}$	$\begin{array}{l} \text{A} \\ \text{B} \end{array} \rightarrow (\text{CH}_3)_2\text{Co}^+(\text{CO})(\text{C}_2\text{H}_5\text{X}) \rightarrow \begin{array}{l} \text{Co}(\text{CO})(\text{C}_2\text{H}_5\text{X})^+ + \text{CH}_4 \\ \text{Co}(\text{C}_2\text{H}_5\text{X})^+ + \text{CH}_4 + \text{CO} \end{array}$	9		3
	$\begin{array}{l} \text{B} \\ \text{C} \end{array} \rightarrow (\text{CH}_3\text{CHO})\text{Co}^+(\text{C}_2\text{H}_5\text{X}) \rightarrow \begin{array}{l} \text{CoC}_2\text{H}_5\text{X}^+ + \text{CH}_3\text{CHO} \\ \text{CoCH}_2\text{CHO}^+ + \text{C}_2\text{H}_5\text{X} \end{array}$	5		12
Reactions Predicted For X- Functional Group				
$\text{Co}^+ + \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}(\text{CH}_3)\text{CH}_2\text{X} \end{array} \rightarrow \begin{array}{l} \text{D} \\ \text{E} \end{array}$	$\begin{array}{l} \text{D} \\ \text{E} \end{array} \rightarrow \begin{array}{l} \text{CoX}^+ + \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}(\text{CH}_3)\text{CH}_2\cdot \\ \text{Co}(\text{C}_2\text{H}_5\text{X})^+ + \text{X}\cdot \end{array} \end{array}$	6	15	4
	$\begin{array}{l} \text{D} \\ \text{E} \end{array} \xrightarrow[\text{Shift}]{\beta\text{-H}} (\text{HX})\text{Co}^+(\text{C}_2\text{H}_5\text{X}) \rightarrow \begin{array}{l} \text{CoHX}^+ + \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}(\text{CH}_3)\text{CH}_2\cdot \\ \text{Co}(\text{C}_2\text{H}_5\text{X})^+ + \text{HX} \end{array} \end{array}$	3		3
	$\begin{array}{l} \text{D} \\ \text{E} \end{array} \xrightarrow[\text{Shift}]{\beta\text{-H}} (\text{HX})\text{Co}^+(\text{C}_2\text{H}_5\text{X}) \rightarrow \begin{array}{l} \text{Co}(\text{C}_2\text{H}_5\text{X})^+ + \text{HX} \end{array}$	35	55	32
Predicted Subsequent Reactions of Intermediate D				
$(\text{HX})\text{Co}^+(\text{C}_2\text{H}_5\text{X}) \rightarrow \begin{array}{l} \text{F} \\ \text{G} \\ \text{H} \end{array}$	$\text{F} \rightarrow (\text{HX})\text{Co}^+(\text{CO})(\text{C}_2\text{H}_5) \rightarrow \begin{array}{l} \text{CoC}_2\text{H}_5^+ + \text{CO} + \text{HX} \\ \text{CoCO}^+ + \text{C}_2\text{H}_5 + \text{HX} \end{array}$	18	30	13
	$\text{G} \rightarrow (\text{HX})\text{Co}^+(\text{C}_2\text{H}_5)(\text{CH}_3\text{CHO})^+ \rightarrow \text{COC}_2\text{H}_5^+ + \text{HX} + \text{CH}_3\text{CHO}$	9		11
	$\text{H} \rightarrow (\text{HX})\text{Co}^+(\text{C}_2\text{H}_5)(\text{CH}_3\text{CHO}) \rightarrow \text{Co}(\text{CO})(\text{C}_2\text{H}_5)^+ + \text{HX} + \text{CH}_3\text{CHO}$	5		
Total of Reaction Products Predicted		93%	100%	78%

the reactions of Co^+ with alkyl halides and alcohols (reactions 1 and 2). After the initial metal insertion process a bond cleavage occurs. We do not observe CoX as a product, presumably due to a unique allyl-like ligand which is formed. This indicates that the observed products are the most stable.



The strength of the R-X bond in the three compounds in Table 27 decreases in the order $\text{OH} > \text{Cl} > \text{Br}$ ($D(\text{R-OH}) = 89.3$ kcal/mole, $D(\text{R-Cl}) = 74.2$ kcal/mole and $D(\text{R-Br}) = 59.9$ kcal/mole.) Thus the reaction



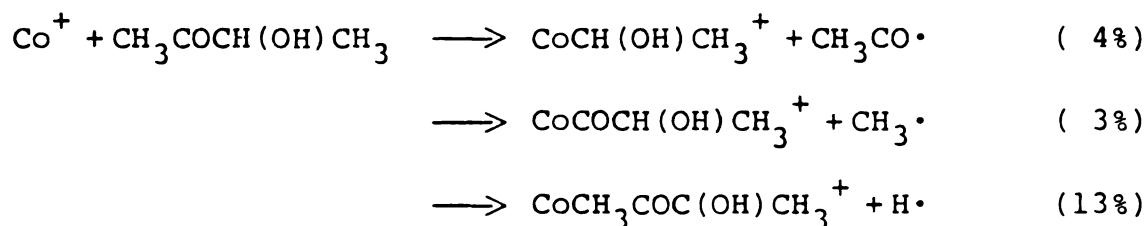
becomes increasingly exothermic in the order $\text{X} = \text{OH}, \text{Cl}, \text{Br}$. Note that the branching ratios reflect this order, with the process becoming more prominent as the reaction becomes more exothermic.

Reactions of Co^+ with 3-bromobutanone are dominated by the bromine atom. This may be due in part to the fact that, for the compounds in Table 27, the weakest C-X bond

is X=Br. Also, the C-Br bond is the weakest bond in 3-bromobutanone, while in 3-chlorobutanone the C-Cl bond strength was about the same as the two C-CO bonds (70-75 kcal/mol). In 3-bromobutanone, the C-Br bond is much weaker and appears to be the preferred site of insertion. This is indicated by the lack of any reactions typical of the ketone group.

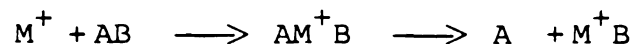
In 3-hydroxybutanone, 78% of the reactions were predictable. The loss of methanol (2%) could be considered as analogous to the loss of CH₃Cl from 3-chlorobutanone.

The remainder of the products of Co⁺ with 3-hydroxybutanone corresponds to the loss of neutral radicals:

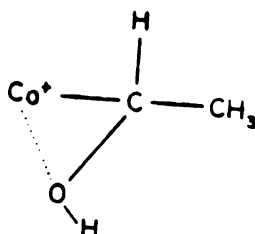


All three products appear to be Co⁺ insertion followed by a bond cleavage. The loss of a radical would be a relatively high energy process, usually much lower energy pathways follow the insertion process (elimination of stable neutrals) as observed in butanone.

The question arises, when would the reaction



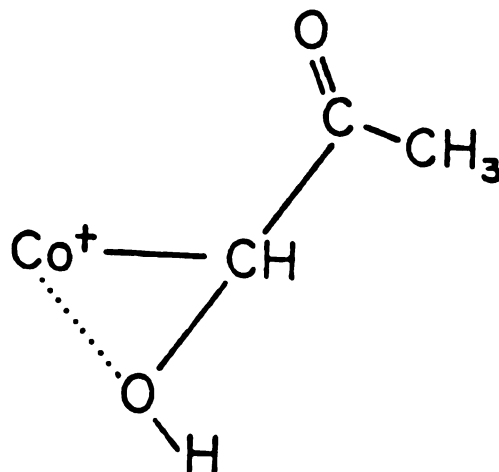
be thermodynamically favored? This would be the case if one or both of the products were unusually stable. If the neutral radical lost was unusually stable these reactions would also be observed for butanone, but they are not. Therefore, the reactions must become prominent due to the nature of the ionic product. M^+B may be unusually stable because the metal-ligand bond strength ($D(M^+-B)$) is high, due to multiple interactions of B with the metal. Note, these reactions only occur with 3-X-butanone where $X=OH$. One would expect the M^+-OH interactions to be stronger than the M^+-Cl, Br . This seems feasible since the fragment of the molecule containing the hydroxy group is always retained. Therefore, it is suggested that the loss of CH_3CO gives the ionic product containing both an M-C σ -bond and a further M-O interaction:



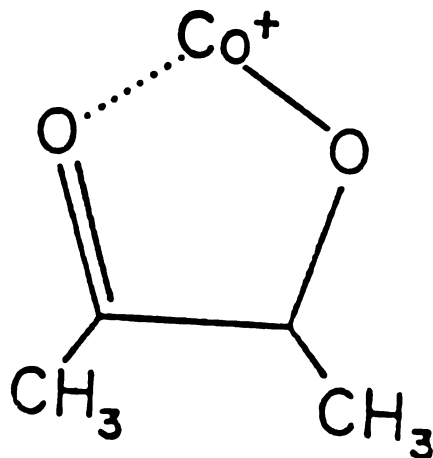
Presumably, the process is observed because $D(Co^+-CH(OH)CH_3) > D(Co^+-C_2H_5)$. To place a lower limit on $D(Co^+-CH(OH)CH_3)$, assuming that the Co^+-C bond strength is approximately the same as the Co^+-CH_3 bond ($D(Co^+-CH_3) = 61 \pm 4$ kcal/mole)[8]. Therefore the additional

($\text{Co}^+ - \text{O}$) interaction must be greater than or equal to 11.3 kcal/mole.

If a β -O can interact with the metal, a similar interaction is proposed in the ionic product of the reaction leading to the loss of CH_3 .



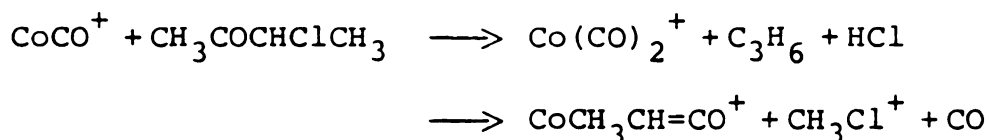
Finally, H-loss could occur via the formation of a five member ring product with the loss of the hydroxyl H.



It is interesting to note that when intermediate D, $\text{Co}(\text{HX})(\text{Butenone})^+$, dissociates, it loses HX when $\text{X}=\text{Cl}$ and Br, but when $\text{X}=\text{OH}$ there is competitive ligand loss which is consistent with what would be predicted from proton affinities, i.e., $\text{D}^\circ(\text{Co}^+-\text{HCl}) < \text{D}^\circ(\text{Co}^+-\text{HBr}) < \text{D}^\circ(\text{Co}^+-\text{H}_2\text{O}) < \text{D}^\circ(\text{Co}^+-\text{CH}_3\text{COCH-CH}_2)$.

B. The Chemistry of CoL_n^+ Ions with 3-Substituted Butanones

The organic rearrangement reactions of CoCO^+ with 3-chlorobutanone are similar to those for Co^+ with loss or retention of the carbonyl. The product of $m/z = 115$ can occur via two pathways:



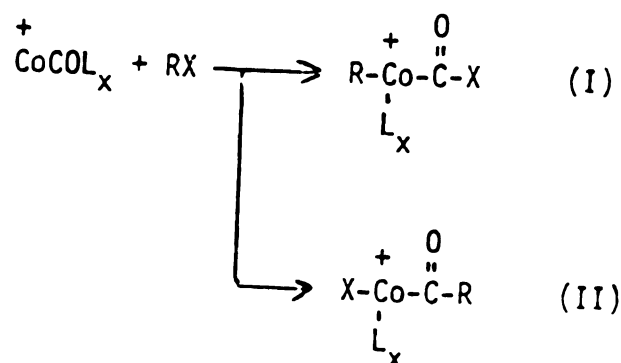
Both pathways are observed in the chemistry of Co^+ and therefore both are likely to occur with CoCO^+ .

As expected the chemistry of $\text{Co}(\text{CO})_2^+$ is reduced due to the lack of empty orbitals on the metal. $\text{Co}(\text{CO})_2^+$ readily loses two CO's (52%) to give sufficient empty orbitals so HCl elimination can occur to give Co^+ -butenone complex.

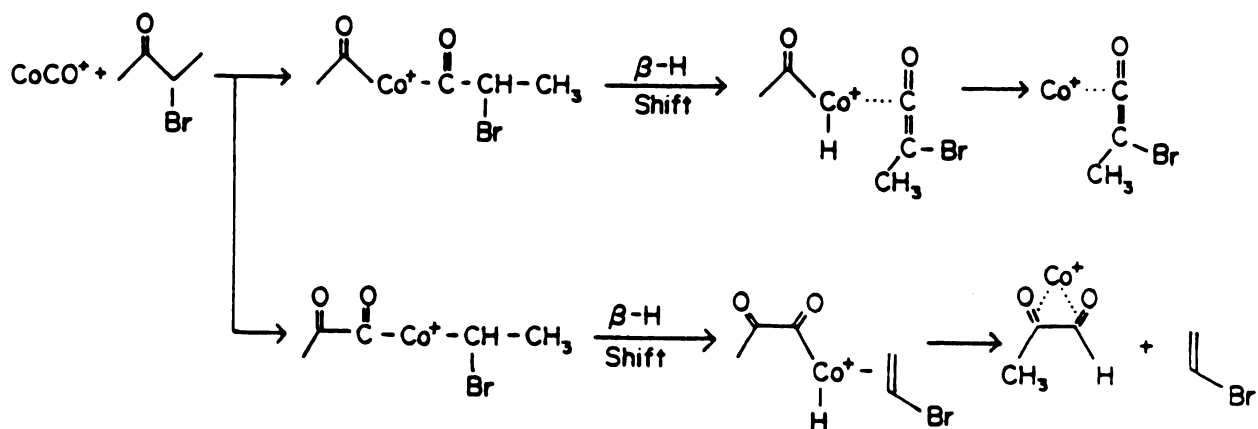
CoNO^+ , as observed in many other cases, is nonreactive but CoCONO^+ and $\text{Co}(\text{CO})_2\text{NO}^+$ react to eliminate CO and HCl

giving a product of the above structure with an additional NO ligand on the metal.

Reactions at the C-Br bond also dominate the chemistry of CoCO^+ with 3-bromobutanone (86%). As discussed in the allyl compounds when the carbonyl ligand actively participates in the insertion process two possibilities exist:



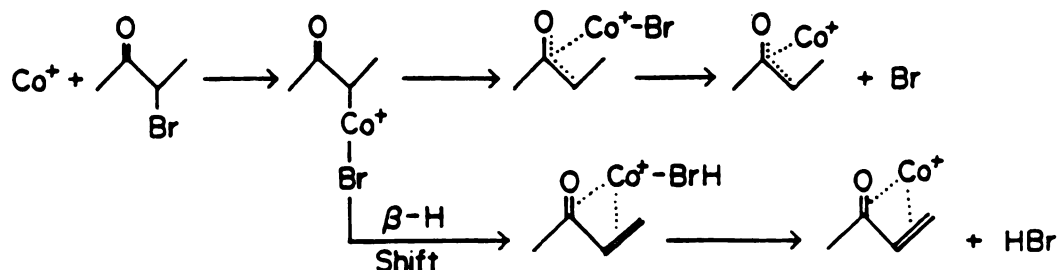
In allyl alcohol the carbonyl prefers the alkyl group (case II). In 3-bromobutanone both pathways occur.



The heat of reaction for the neutral organic molecule to undergo the above reaction with CO has been calculated to be 28.35 kcal/mole. This is of the same magnitude of most other ion/molecule reactions. Most likely the initial complexation of the CoCO^+ with the substituted ketone provides this energy. Also the feasibility of obtaining a Co^+ -(butadiene-like) complex plays a role in this reaction.

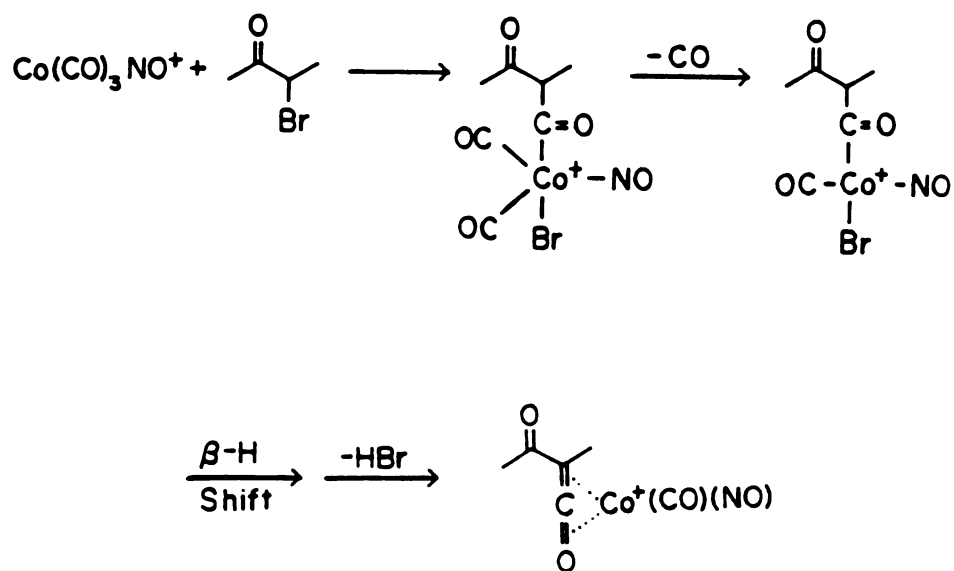
The former reaction is also the predominant reaction for $\text{Co}(\text{CO})_2^+$ (74%). The remaining reactions are the elimination of CO and HBr.

In 3-bromobutanone, direct evidence for Co^+ insertion into C-Br bond is observed.



CoBr^+ is not observed which is also indicative of a weak Co^+-Br bond. CoCONO^+ reacts to eliminate HBr with the loss of a CO. $\text{Co}(\text{CO})_2\text{NO}^+$ doesn't give this elimination

but $\text{Co}(\text{CO})_3\text{NO}^+$ eliminated one or two CO's and a HBr. This indicates that a CO ligand actively participates in the chemistry via CoCO^+ insertion into the C-Br bond where the CO prefers the alkyl group. After insertion, a CO from the complex is lost. This provides an empty orbital so a β -H atom shift may occur resulting in the elimination of HBr.



Due to low resolution and signal intensity on higher mass ions, confirmation of ligand substitution reactions was not obtainable in this mixture. Ions appearing at m/z corresponding to the ligand substitution processes were observed however.

The reactions of CoCO^+ and $\text{Co}(\text{CO})_2^+$ with 3-hydroxybutanone resemble those of Co^+ with the number of reactions reduced for the $\text{Co}(\text{CO})_2^+$ ion. Reactions of $\text{Co}(\text{CO})_x\text{NO}^+$ ions are typically dominated by ligand

substitution processes, but the rearrangement processes which are present are dominated by the ketone functionality due to the weaker C-CO bonds rather than at the C-OH bond.

CHAPTER 9

THE CHEMISTRY OF COBALT-CONTAINING IONS WITH SUBSTITUTED CARBOXYLIC ACIDS

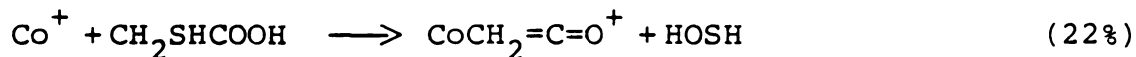
A. Reaction of Co^+ with Substituted Carboxylic Acids

These results will be presented for a given skeletal chain with various second functional group ($\text{X} = \text{Cl}, \text{Br}, \text{OH}, \text{SH}$).

1. The Chemistry of Co^+ with Substituted Acetic Acid

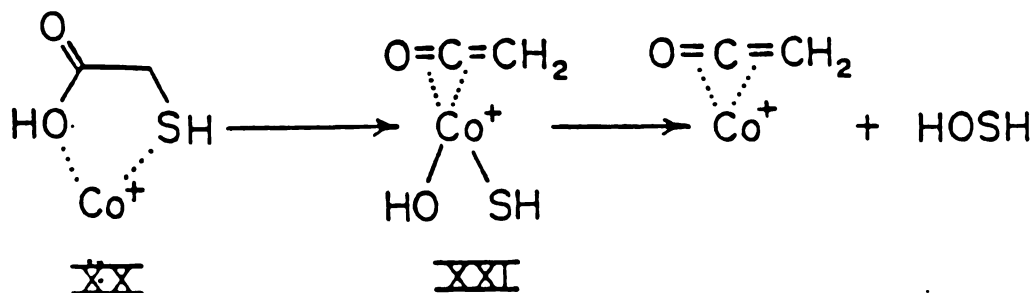
Table 28 contains the predicted reactions and the branching ratios for the observed reactions for chloro, bromo, hydroxy and mercapto acetic acids. All predicted products are those expected for acids. No products for the second functional group are suggested in Table 28 since, if Co^+ inserts into the C-X bond, there is no $\beta\text{-H}$ available. The only products that would be predicted would correspond to X-abstraction, however in no case was this observed. The reactions observed are dominated by the chemistry of the COOH group, more specifically insertion into the CO-OH bond.

There are two reactions observed for 2-mercaptoacetic acid reacting with Co^+ that were not predicted.

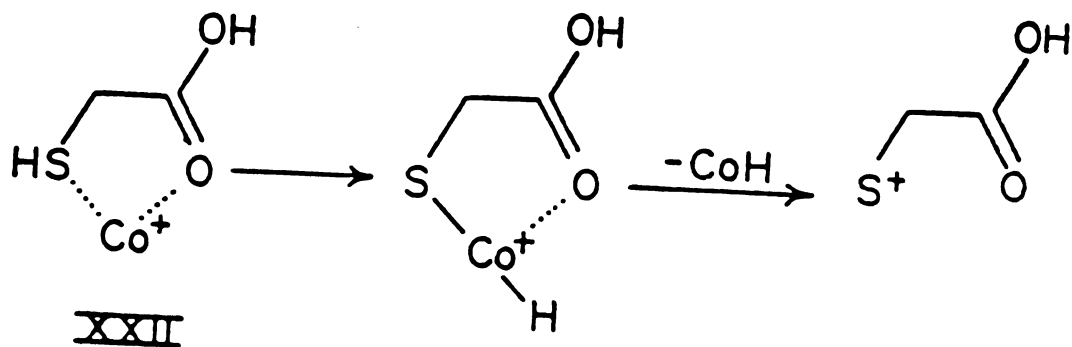


These reactions involve Co^+ forming a five member ring between the S and either the hydroxyl group (structure **XX**) or the carbonyl oxygen (structure **XXII**).

The first cyclic intermediate (structure **XX** is similar to the cyclic intermediate proposed for the reaction of Co^+ with 2-chloroethanol [4]. From this intermediate cleavage of the C-SH and CO-OH bond occurs to give an intermediate, structure **XXI**, which then loses HOSH. There is a possibility that this product exists as two radicals, OH and SH. In doing so, a higher energetic pathway is involved. (Note, HSOH, hydrogen thioperoxide, has been observed previously by Smardzewski and Lin in an argon matrix isolation studies [50].)



Eleven percent of the products correspond to the loss of CoH, i.e., formation of $(M-1)^+$. In the chemistry of Co^+ with thiols and carboxylic acids, the formation of CoH was not observed in any case. Therefore, in order to observe this reaction product for this acid there must be interaction of Co^+ with both groups which causes this reaction to occur. The proton affinity of thiols are greater than the corresponding alcohol. Therefore the presence of the SH group breaks the dominating effect of the Co^+ -acid group interaction (structure XVIII). This leads to the formation of the cyclic intermediate XXII.

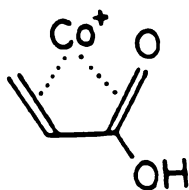


From this intermediate metal insertion into the S-H bond can occur followed by a charge transfer. This type of reaction is not observed in the 2-hydroxyacetic acid and may be related to the fact that the O-H bond is 15 kcal/mole stronger than the S-H bond in the thiol acid. It is interesting to note the similarity between this reaction and the elimination of H• from 3-hydroxybutanone. If it goes through the intermediates proposed for the hydroxyl

ketone and thiol acid, cleavage of the $\text{Co}^+\text{-H}$ bond is observed for the ketone. However, in the thiol acid, a charge transfer and loss of CoH is observed. This is consistent with the fact that sulfur containing compounds have, in general, lower ionization potentials than the oxygen containing analogs. Therefore, loss of CoH is not unexpected for R-SH while not observed for R-OH .

2. The Chemistry of Co^+ with 2-Substituted Propanoic Acids

In two of the three compounds studied ($\text{X}=\text{Cl}, \text{SH}$) all of the reaction products were predicted (see Table 29) based on what is known of the chemistry of Co^+ with alkyl halides, thiols, and propanoic acid. Several points to be noticed: first, elimination of HX was observed to a good degree. Insertion by Co^+ into the C-X bond gave a species from which a $\beta\text{-H}$ shift can readily occur to give $\text{Co}(\text{HX})$ (propanoic acid) $^+$ which loses the HX to give product where the Co^+ interacts with the resulting bonds which is similar to a $\text{Co}^+\text{-butadiene}$ complex.

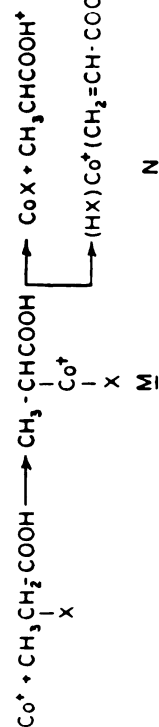


Second, retention of water is favored over retention of the substituted ketene. Similar results, i.e. retention

Table 29 Predicted Reactions For Co^+ With 2-X - Propanoic Acids

Reactions Predicted For Acid Group	% Observed		
	X=Cl	X=Br	X=SH
$\text{Co}^+ + \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{COOH} \xrightarrow{\text{O}} \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{C}(=\text{O}) - \text{OH} \xrightarrow{\text{O}} \text{Co}(\text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{C}(=\text{O}))^+ + \text{H}_2\text{O}$			
$\text{Co}^+ + \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{COOH} \xrightarrow{\text{O}} \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{C}(=\text{O}) - \text{OH} \xrightarrow{\text{O}} \text{CoH}_2\text{O}^+ + \text{CH}_3 - \text{CX} = \text{C} = \text{O}$	49		21
$\text{Co}^+ + \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{COOH} \xrightarrow{\text{O}} \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{C}(=\text{O}) - \text{OH} \xrightarrow{\text{O}} (\text{CH}_3\text{CHX})\text{Co}^+(\text{CO})(\text{H}_2\text{O}) \xrightarrow{\text{O}} \text{Co}(\text{C}_2\text{H}_3\text{X})(\text{H}_2\text{O})^+ + \text{CO}$			
$\text{Co}^+ + \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{COOH} \xrightarrow{\text{O}} \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{C}(=\text{O}) - \text{OH} \xrightarrow{\text{O}} (\text{C}_2\text{H}_3\text{X})\text{Co}^+(\text{HCOOH}) \xrightarrow{\text{O}} \text{CoHCOOH}^+ + \text{C}_2\text{H}_3\text{X}$	3		41
$\text{Co}^+ + \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{COOH} \xrightarrow{\text{O}} \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{C}(=\text{O}) - \text{OH} \xrightarrow{\text{O}} \text{CoC}_2\text{H}_3\text{X}^+ + \text{HCOOH}$			
$\text{Co}^+ + \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{COOH} \xrightarrow{\text{O}} \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{C}(=\text{O}) - \text{OH} \xrightarrow{\text{O}} \text{CoX} + \text{CH}_3\text{CHCOOH}^+$			
$\text{Co}^+ + \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{COOH} \xrightarrow{\text{O}} \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{C}(=\text{O}) - \text{OH} \xrightarrow{\text{O}} (\text{HX})\text{Co}^+(\text{CH}_2 = \text{CH} - \text{COOH})^+ \xrightarrow{\text{O}} \text{CoHX}^+ + \text{C}_3\text{H}_4\text{O}_2$			
$\text{Co}^+ + \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{COOH} \xrightarrow{\text{O}} \text{CH}_3 - \underset{\text{X}}{\text{CH}} - \text{C}(=\text{O}) - \text{OH} \xrightarrow{\text{O}} (\text{HX})\text{Co}^+(\text{CH}_2 = \text{CH} - \text{COOH})^+ \xrightarrow{\text{O}} \text{Co}(\text{CH}_2 = \text{CH} - \text{COOH})^+ + \text{HX}$	48		38
Total of Reaction Products Predicted	100%	0%	100%

Reaction Prediction For X- Functional Group



of H_2O over ketenes as ligands, are observed in the unsubstituted acids. Third, insertion into both sides of the carbonyl group is observed to give products typical of the acid. From the type of reactions occurring and the branching ratios, it has been observed that Co^+ prefers to attack at the acid functional group more than at Cl or SH.

In 2-bromopropanoic acid, none of the predicted reactions of Co^+ were observed. In fact, no reactions of Co^+ with 2-bromopropanoic acid were observed. At present, there is no explanation for this lack of reactivity.

3. Reactions of Co^+ with 3-Substituted Propanoic Acids

Table 30 shows that the ability to predict the products of the reactions of Co^+ with this series of compounds varies from 47% to 100%. In 3-hydroxypropanoic acid, all reactions were predicted but the exact pathway and product structures could not be determined. Two products, CoH_2O^+ and $\text{CoC}_3\text{H}_4\text{O}_2^+$, $(\text{Co}(\text{M}-\text{H}_2))^+$, can be formed either through reactions at the OH group, that is alcohol-like reactions, or through reactions typical of acids by attack at the -COOH group. Attack at either group would yield products of the same formula therefore the branching ratios are given for the total product regardless of the structure.

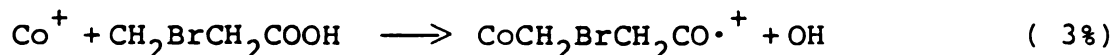
In 3-bromopropanoic acid, 29% of the reaction products are due to primary rearrangement of the intact molecule,

Table 30 Predicted Reactions For Co^+ With 3-X-Propanoic Acids

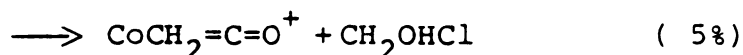
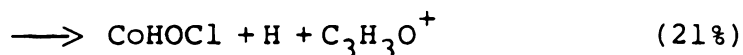
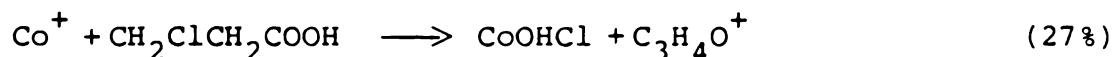
Reactions Predicted For Acid Group		% Observed		
		X=Cl	X=Br	X=OH
$\text{Co}^+ + \text{CH}_2\text{CH}_2\text{COOH} \xrightarrow{\text{X}} \text{CH}_2\text{CH}_2\text{Co}^+-\text{C}(=\text{O})-\text{OH} \xrightarrow{\text{X}} (\text{C}_2\text{H}_5\text{X})\text{Co}^+(\text{HCOOH}) \xrightarrow{\text{X}} \text{CoC}_2\text{H}_5\text{X}^+ + \text{HCOOH}$ $\xrightarrow{\text{X}} \text{CoHCOOH}^+ + \text{C}_2\text{H}_5\text{X}$		5		51
				10
$\text{Co}^+ + \text{CH}_2\text{CH}_2\text{COOH} \xrightarrow{\text{X}} \text{CH}_2\text{CH}_2\text{Co}^+-\text{C}(=\text{O})-\text{OH} \xrightarrow{\text{X}} (\text{CH}_2\text{CH}=\text{C}=\text{O})\text{Co}^+(\text{H}_2\text{O})^+ \xrightarrow{\text{X}} \text{CoH}_2\text{O} + \text{CH}_2\text{XCH}=\text{C}=\text{O}$ $\xrightarrow{\text{X}} \text{Co}(\text{CH}_2\text{XCH}=\text{C}=\text{O})^+ + \text{H}_2\text{O}$			2	(14) ^a
				(25) ^a
Reactions Predicted For X Functional Group				
$\text{Co}^+ + \text{CH}_2\text{CH}_2\text{COOH} \xrightarrow{\text{X}} \text{CH}_2\text{CH}_2\text{COOH} \xrightarrow{\text{X}} (\text{HX})\text{Co}^+(\text{CH}_2=\text{CHCOOH}) \xrightarrow{\text{X}} \text{CoHX}^+ + \text{CH}_2=\text{CHCOOH}$ $\xrightarrow{\text{X}} \text{Co}(\text{CH}_2=\text{CHCOOH})^+ + \text{HX}$		4	27	(14) ^a
				(25) ^a
Subsequent Reaction Products Predicted For Intermediate Q				
$(\text{HX})\text{Co}^+(\text{CH}_2=\text{CHCOOH}) \xrightarrow{\text{X}} \text{CoCO}(\text{HX})^+ + \text{CH}_2\text{CHOH}$ $\xrightarrow{\text{X}} \text{CoCH}_2\text{CHX}^+ + \text{HX} + \text{CO}$ $\xrightarrow{\text{X}} \text{CoC}_2\text{H}_2^+ + \text{HX} + \text{HCOOH}$		28	62	
		10		
Total of Reaction Products Predicted		47%	97%	100%

a) These two products, CoH_2O^+ and $\text{CoC}_2\text{H}_4\text{O}_2^+$ may be formed via two different pathways, both of which are likely to occur.

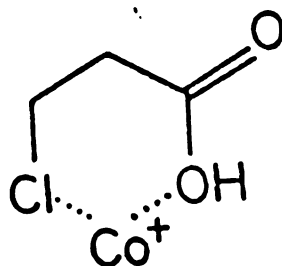
68% of the products result from subsequent rearrangement of the $\text{Co}(\text{HBr})(\text{propenoic acid})^+$ intermediate. From this intermediate insertion into the $\text{Co}-\text{OH}$ occurs followed by a β -alkyl shift and rearrangement to give either $\text{Co}(\text{HBr})(\text{CO})^+$ (6%) or $\text{Co}(\text{CH}_2\text{CHOH})^+$ (62%). The remaining 3% of the reactions in this mixture involves insertion into the $\text{CO}-\text{OH}$ bond by the Co^+ followed by cleavage of the Co^+-OH bond.



The reactions observed for Co^+ and 3-chloropropanoic acid are due primarily to reactions of each functional group directly or from an intermediate similar to what was discussed for bromopropanoic acid. The following reactions were not predicted for this mixture:

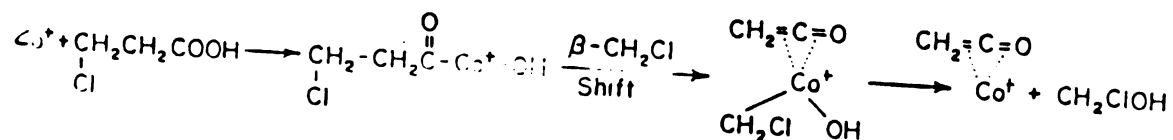


The first reaction can occur when Co^+ interacts with the Cl and the OH groups simultaneously giving a six member ring intermediate.



followed by bond cleavage/charge transfer process to yield CoOHCl as the neutral lost in this reaction. One possible structure for the product ion is $\text{CH}_2=\text{CH}-\text{CHO}^+$, the acrolein molecular ion. In the electron impact mass spectrum of acrolein a large $(\text{M}-\text{H})^+$ ion is observed [48]. Therefore if the product from the loss of Cl and OH resemble acrolein one would expect to see a loss of H to give the $\text{C}_3\text{H}_3\text{O}^+$ product.

Also, Co^+ reacts with 3-chloropropanoic acid to eliminate chloromethanol. Propanoic acid does not eliminate the corresponding alcohol, methanol. After insertion of Co^+ in the $\text{CO}-\text{OH}$ bond, instead of $\beta\text{-H}$ atom shift a $\beta\text{-CH}_2\text{Cl}$ shift may occur. The presence of the chlorine atom weakens the $\text{C}_2\text{-C}_3$ bond ($D(\text{CH}_3\text{-CH}_2\text{COOH}) \approx 83 \text{ kcal/mole}$, $D(\text{CH}_2\text{Cl-CH}_2\text{COOH}) \approx 77.9 \text{ kcal/mole}$) thereby, making the C-C bond more accessible for Co^+ insertion, which would then shift to the metal, resulting in the elimination of the substituted alcohol.



B. The Chemistry of CoL_n^+ with Substituted Carboxylic Acids. Ligand Effects.

1. The Chloro-Acids

In Tables 31-33 are the reactions of each metal containing ion with the chloroacids. Also in these tables are the branching ratios.

In an earlier section, the chemistry of Co^+ with 2-chloropropanoic acid was discussed in terms of the predictability of the reactions. As seen in Table 32 the reactions of CoCO^+ with this acid follow those of Co^+ with attack at the C-Cl bond being favored more than attack at the acid group. The chemistry of $\text{Co}(\text{CO})_2^+$ is dominated by ligand substitution (82%). The remaining 18% of the reactions of $\text{Co}(\text{CO})_2^+$ is attacked by the metal-containing ion at the bonds on both sides of the carbonyl of the acid group.

Reactions of the $\text{Co}(\text{CO})_n\text{NO}^+$ ion are also what one may expect from earlier discussions, that is, CoNO^+ is nonreactive and ligand substitution predominates the

Table 31. The Reactions of cobalt containing ions with 2-chloroacetic acid ($M = CH_2ClCOOH$).

$Co^+ + M \longrightarrow$	$CoH_2O^+ + CHCl=C=O$	(52%)
	$\longrightarrow CoCHCl=C=O^+ + H_2O$	(48%)
$CoCO^+ + M \longrightarrow$	$CoM^+ + CO$	(24%)
	$\longrightarrow CoH_2O^+ + CHCl=C=O + CO$	(48%)
	$\longrightarrow CoCOH_2O^+ + CHCl=C=O$	(5%)
	$\longrightarrow CoCHCl=C=O^+ + H_2O + CO$	(8%)
	$\longrightarrow Co(M-HCl)^+ + HCl + CO$	(2%)
	$\longrightarrow CoCH_2ClCH^+ + 2CO$	(13%)
$Co(CO)_2^+ + M \longrightarrow$	$CoM^+ + 2CO$	(20%)
	$\longrightarrow CoCOM^+ + CO$	(38%)
	$\longrightarrow CoCOH_2O^+ + CHCl=C=O + CO$	(42%)
$CoNO^+ + M \longrightarrow$	$CoNOH_2O^+ + CHCl=C=O$	(100%)
$CoCONO^+ + M \longrightarrow$	$CoNOM^+ + CO$	(11%)
	$\longrightarrow CoNOH_2O^+ + CHCl=C=O + CO$	(89%)
$Co(CO)_2NO^+ + M \longrightarrow$	$CoCONOM^+ + CO$	(6%)
	$\longrightarrow CoNOM^+ + 2CO$	(42%)
	$\longrightarrow CoCONOH_2O^+ + CHClCO + CO$	(52%)
$Co(CO)_3NO^+ + M \longrightarrow$	$CoNOCOM^+ + 2CO$	(67%)
	$\longrightarrow CoCONOH_2O^+ + CHClCO + CO$	(33%)

Table 32. The reactions of cobalt containing ions with 2-chloropropanoic acid ($M = CH_3CHClCOOH$).

<hr/>		
Co^+	$+ M \longrightarrow CoH_2O^+ + CH_3CCl=C=O$	(48%)
	$\longrightarrow CoHCOOH^+ + C_2H_3Cl$	(4%)
	$\longrightarrow Co(CH_2=CHCOOH)^+ + HCl$	(48%)
$CoCO^+$	$+ M \longrightarrow CoCOH_2O^+ + CH_3CCl=C=O$	(5%)
	$\longrightarrow CoCOH_2O^+ + CH_3CCl=C=O/$ $CoHCOOH^+ + C_2H_3Cl + CO$	(48%)
	$\longrightarrow Co(M-HCl)^+ + HCl + CO$	(62%)
	$\longrightarrow CoCO(M-HCl)^+ + HCl$	(9%)
	$\longrightarrow CoCOHCOOH^+ + C_2H_3Cl$	(13%)
$Co(CO)_2^+$	$+ M \longrightarrow CoM^+ + 2CO$	(32%)
	$\longrightarrow CoCOM^+ + CO$	(50%)
	$\longrightarrow CoCOH_2O^+ + CH_3CClCO + CO/$ $CoHCOOH^+ + C_2H_3Cl + 2CO$	(14%)
	$\longrightarrow Co(CO)_2HCOOH^+ + C_2H_3Cl$	(4%)
$CoNO^+$	$+ M \longrightarrow$ No Reaction	
$CoCONO^+$	$+ M \longrightarrow CoNOM^+ + CO$	(35%)
	$\longrightarrow CoNOH_2O^+ + CH_3CClCO + CO$	(59%)
	$\longrightarrow CoNOCOHOHCOOH^+ + C_2H_3Cl$	(6%)
<hr/>		

Table 32 Continues.

Table 32 Continued.

$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 2\text{CO}$	(62%)
	$\longrightarrow \text{CoCONOH}_2\text{O}^+ + \text{CH}_3\text{CClCO} + \text{CO}$	(16%)
	$\longrightarrow \text{CoNOCOHC}\text{OOH}^+ + \text{C}_2\text{H}_3\text{Cl}$	(7%)
	$\longrightarrow \text{CoNOCH}_2\text{ClCOHC}\text{OOH}^+ + \text{CH}_2\text{CO} + \text{CO}$	(13%)
	$\longrightarrow \text{Co}(\text{CO})_2\text{NOHC}\text{OOH}^+ + \text{C}_2\text{H}_3\text{Cl}$	(2%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 3\text{CO}$	(15%)
	$\longrightarrow \text{CoNOCOM}^+ + 2\text{CO}$	(64%)
	$\longrightarrow \text{CoCONOH}_2\text{O}^+ + \text{CHClCO} + \text{CO}$	(2%)
	$\longrightarrow \text{Co}(\text{CO})_2\text{NOHC}\text{OOH}^+ + \text{C}_2\text{H}_3\text{Cl} + \text{CO}$	(8%)
	$\longrightarrow \text{CoCONOHC}\text{OOH}^+ + \text{C}_2\text{H}_3\text{Cl} + 2\text{CO}$	(11%)

Table 33. The reactions of cobalt containing ions with 3-chloropropanoic acid ($M = CH_2ClCH_2COOH$).

$Co^+ + M \longrightarrow$	$CoCH_2=CHCOOH^+ + HCl$	(4%)
\longrightarrow	$CoC_2H_2^+ + HCl + HCOOH$	(10%)
\longrightarrow	$CoC_2H_3Cl^+ + HCOOH$	(5%)
\longrightarrow	$C_3H_4O^+ + CoOHC1$	(27%)
\longrightarrow	$C_3H_3O^+ + CoOHC1 + H$	(21%)
\longrightarrow	$CoCH_2CHOH^+ + HCl + CO$	(28%)
\longrightarrow	$CoCH_2=C=O^+ + CH_2OHC1$	(5%)
$CoCO^+ + M \longrightarrow$	$CoM^+ + CO$	(19%)
\longrightarrow	$CoH_2O^+ + CH_2ClCHCO + CO$	(42%)
\longrightarrow	$Co(M-HCl)^+ + HCl + CO$	(33%)
\longrightarrow	$CoCO(M-HCl)^+ + HCl$	(4%)
\longrightarrow	$CoC_2H_3Cl^+ + HCOOH + CO$	(1%)
\longrightarrow	$CoCOHCOOH^+ + C_2H_3Cl$	(1%)
$Co(CO)_2^+ + M \longrightarrow$	$CoM^+ + 2CO$	(78%)
\longrightarrow	$CoCOM^+ + CO$	(11%)
\longrightarrow	$CoCO(M-HCl)^+ + HCl + CO$	(10%)
$CoNO^+ + M \longrightarrow$	No Reaction	
$CoCONO^+ + M \longrightarrow$	$CoNO(M-HCl)^+ + HCl + CO$	(100%)

Table 33 Continues.

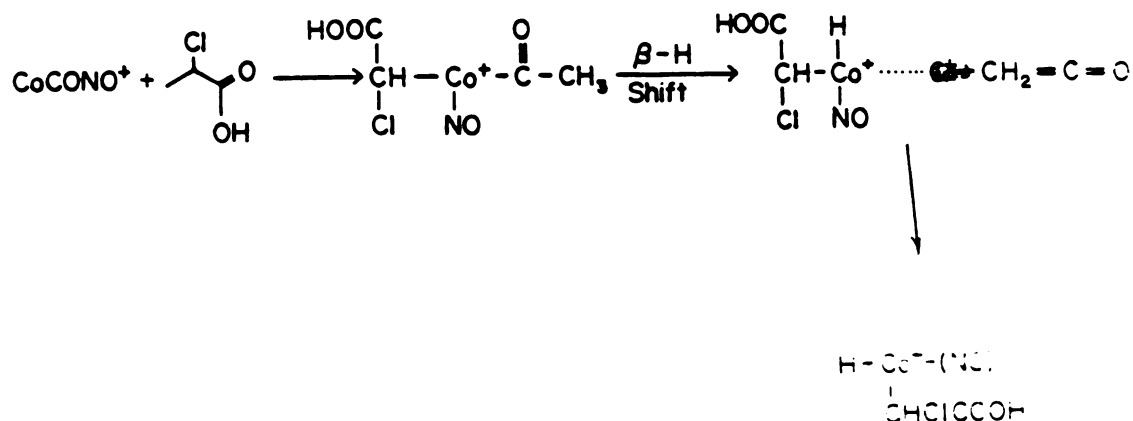
Table 33 Continued.

$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoCONOM}^+ + \text{CO}$	(76%)
\longrightarrow	$\text{CoNO}(\text{M-HCl})^+ + \text{HCl} + 2\text{CO}$	(16%)
\longrightarrow	$\text{CoCONOH}_2\text{O}^+ + \text{CH}_2\text{ClCH}=\text{C}=\text{O}$	(8%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOCOM}^+ + 2\text{CO}$	(62%)
\longrightarrow	$\text{CoCONOH}_2\text{O}^+ + \text{CHClCO} + \text{CO}$	(24%)
	$\text{CoNOHCOOH}^+ + \text{C}_2\text{H}_3\text{Cl} + 3\text{CO}$	
\longrightarrow	$\text{CoCONO}(\text{M-HCl})^+ + \text{HCl} + 2\text{CO}$	(14%)

Table 34. The Reactions of cobalt containing ions with
2-bromoacetic acid ($M = \text{CH}_2\text{BrCOOH}$).

$\text{Co}^+ + M \longrightarrow \text{CoCHBr}=\text{C}=\text{O}^+ + \text{H}_2\text{O}$	(100%)
$\text{CoCO}^+ + M \longrightarrow \text{CoM}^+ + \text{CO}$	(74%)
$\longrightarrow \text{CoCHBr}=\text{C}=\text{O}^+ + \text{H}_2\text{O} + \text{CO}$	(26%)
$\text{Co}(\text{CO})_2^+ + M \longrightarrow \text{CoCHBr}=\text{C}=\text{O}^+ + \text{H}_2\text{O} + 2\text{CO}$	(100%)
$\text{CoNO}^+ + M \longrightarrow \text{No Reaction}$	
$\text{CoCONO}^+ + M \longrightarrow \text{CoNOM}^+ + \text{CO}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+ + M \longrightarrow \text{CoNOM}^+ + 2\text{CO}$	(100%)
$\text{Co}(\text{CO})_3\text{NO}^+ + M \longrightarrow \text{CoCONOM}^+ + 2\text{CO}$	(100%)

chemistry of the other ions. There is one new reaction which involves insertion of a CoCO^+ into a C-C bond, followed by a β -H atom shift then ligand loss process to give $\text{CoNO}(\text{CH}_2\text{ClCOOH})^+$.



All the reactions involving the loss of the cobalt atom that was observed for the reactions of Co^+ with 3-chloropropanoic acid are not observed once a ligand is placed on the metal. This is because CoCO has a higher ionization potential than that of Co ($\text{IP}(\text{Co}) = 7.87 \text{ eV}$ and $\text{IP}(\text{CoCO}) = 16.5 \text{ eV}$) [43]. Other than the ligand substitution reactions, the chemistry of the CoL_n^+ ions are dominated by attack at the chlorine atom. What is interesting to note is that attack at the C-OH bond (to give $\text{Co}(\text{water})^+$ type products) is observed in these ions while absent in Co^+ .

2. The Bromo-Acids

In Tables 34-36 are the reactions of each metal-containing ion with the bromoacids. Also in these tables are the branching ratios.

Table 35. The reactions of cobalt containing ions with 2-bromopropanoic acid ($M = CH_3CHBrCOOH$).

$Co^+ + M \longrightarrow$ No Reaction		
$CoCO^+ + M \longrightarrow$	$CoCOH_2O^+ + CH_3CBr=C=O$	(22%)
\longrightarrow	$CoH_2O^+ + CH_3CBr=C=O + CO$	(28%)
\longrightarrow	$Co(M-HBr)^+ + HBr + CO$	(41%)
\longrightarrow	$CoCO(M-HBr)^+ + HBr$	(9%)
$Co(CO)_2^+ + M \longrightarrow$	$CoCOM^+ + CO$	(22%)
\longrightarrow	$CoCOH_2O^+ + CH_3CBr=C=O + CO$	(78%)
$CoNO^+ + M \longrightarrow$ No Reaction		
$CoCONO^+ + M \longrightarrow$	$CoNOM^+ + CO$	(14%)
\longrightarrow	$CoNO(M-HBr)^+ + HBr + CO$	(55%)
\longrightarrow	$CoNOH_2O^+ + CH_3CBrCO + CO$	(31%)
$Co(CO)_2NO^+ + M \longrightarrow$	$CoNOM^+ + 2CO$	(51%)
\longrightarrow	$CoCONOH_2O^+ + CH_3CBrCO + CO$	(27%)
\longrightarrow	$CoNOH_2O^+ + CH_3CBrCO + 2CO$	(22%)
$Co(CO)_3NO^+ + M \longrightarrow$	$CoNOM^+ + 3CO$	(78%)
\longrightarrow	$Co(CO)_2NOH_2O^+ + CH_3CBrCO + CO$	(22%)

Table 36. The reactions of cobalt containing ions with
3-bromopropanoic acid ($M = CH_2BrCH_2COOH$).

$Co^+ + M \longrightarrow$	$Co(M-HBr)^+ + HBr$	(27%)
\longrightarrow	$CoCH_2CHOH^+ + HBr + CO$	(62%)
\longrightarrow	$Co(M-OH)^+ + OH$	(3%)
\longrightarrow	$Co(CO)HBr^+ + CH_2CHOH$	(6%)
\longrightarrow	$CoH_2O^+ + CH_2BrCH=C=O$	(2%)
$CoCO^+ + M \longrightarrow$	$CoM^+ + CO$	(25%)
\longrightarrow	$Co(M-HBr)^+ + HBr + CO$ / $CoCO(CH_2=CHOH)^+ + HBr + CO$	(36%)
\longrightarrow	$CoCO(M-HBr)^+ + HBr$	(4%)
\longrightarrow	$CoCH_2CHOH^+ + HBr + 2CO$	(17%)
\longrightarrow	$CoCOHBr^+ + CH_2CHOH + CO$	(2%)
\longrightarrow	$CoH_2O^+ + CH_2BrCHCO + CO$	(5%)
\longrightarrow	$CoCOH_2O^+ + CH_2BrCHCO$	(11%)
$Co(CO)_2^+ + M \longrightarrow$	$CoM^+ + 2CO$	(35%)
\longrightarrow	$CoCO(M-HBr)^+ + HBr + CO$ / $Co(CO)_2CH_2CHOH^+ + HBr + CO$	(1%)
\longrightarrow	$Co(M-HBr)^+ + HBr + 2CO$ $CoCO(C_2H_3OH)^+ + HBr + 2CO$	(31%)
\longrightarrow	$CoCH_2CHOH^+ + HBr + 3CO$	(17%)
\longrightarrow	$CoCO(HBr)^+ + CH_2CHOH + 2CO$	(2%)
\longrightarrow	$CoCOH_2O^+ + CH_2BrCHCO + CO$	(14%)

Table 36 Continues.

Table 36 Continued.

$\text{CoNO}^+ + \text{M} \longrightarrow$	$\text{CoNO}(\text{M-HBr})^+ + \text{HBr}$	(100%)
$\text{CoCONO}^+ + \text{M} \longrightarrow$	$\text{CoNO}(\text{M-HBr})^+ + \text{HBr}$	(100%)
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(96%)
	$\longrightarrow \text{CoNO}(\text{M-HBr})^+ + \text{HBr} + 3\text{CO}$	(3%)
	$\longrightarrow \text{CoCONO}(\text{M-HBr})^+ + \text{HBr} + 2\text{CO}$	(1%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNO}(\text{M-HBr})^+ + \text{HBr} + 3\text{CO}$	(67%)
	$\longrightarrow \text{CoCONO}(\text{M-HBr})^+ + \text{HBr} + 2\text{CO}$	(33%)

Co^+ reacted with bromoacetic via insertion into the C-OH bond with the loss of water after a β -H atom shift. This reaction also occurs with CoCO^+ and $\text{Co}(\text{CO})_2^+$ with the loss of all CO's from the metal giving the $\text{Co}(\text{CHBr}=\text{C}=\text{O})^+$ ion as the sole product. $\text{Co}(\text{CO})_n\text{NO}^+$ ions react only via ligand substitution.

The reactions of CoCO^+ and $\text{Co}(\text{CO})_2^+$ with 2-bromopropanoic acid is richer than Co^+ . As pointed out previously Co^+ does not react with this acid. The reactions of CoCO^+ are divided equally between attack at the CO-OH bond and the C-Br bond.

The reactions of CoCO^+ and $\text{Co}(\text{CO})_2^+$ are similar to Co^+ with 3-bromopropanoic acid. Attack at the C-Br bond to eliminate HBr and a number of carbonyls is dominant reaction pathway. In the chemistry of Co^+ with this acid it was noted that the elimination of both HBr and CO occurred (via successive reactions). This also occurs for both of these ions. CoCO^+ reacts with 3-bromopropanoic acid to eliminate two CO's and HBr to form $\text{Co}(\text{CH}_2=\text{CHOH})^+$. The product corresponding to the loss of one CO and HBr can have two possible structures: $\text{Co}(\text{2-propenoic acid})^+$ or $\text{CoCO}(\text{CH}_2=\text{CHOH})^+$. Similar product structures are also possible for the reactions of $\text{Co}(\text{CO})_2^+$.

$\text{Co}(\text{CO})_n\text{NO}^+$ ions react to eliminate HBr from this acid. CoNO^+ also reacts to eliminate HBr. This can serve as evidence that the carbonyls do not participate in the reactions. In order for the elimination of HBr to occur

from $\text{Co}(\text{CO})_2\text{NO}^+$ and $\text{Co}(\text{CO})_3\text{NO}^+$ ions, the elimination of at least one CO must occur to give a sufficient number of empty orbitals on the metal to allow insertion and β -H atom shift. Elimination of CO's remove much of the excess internal energy of an activated complex. Therefore the most likely rearrangement to CO and vinyl alcohol does not occur.

3. The Hydroxy-Acids

In Tables 37 and 38 are the reactions of each metal-containing ion with the hydroxyacids. Also in these tables are the branching ratios.

The Co^+ , CoCO^+ and $\text{Co}(\text{CO})_2^+$ all react with 2-hydroxyacetic acid to give $\text{CoCHOH}=\text{C}=\text{O}^+$. In CoCO^+ , 98% of the reaction is due to ligand substitution and the remainder leads to the formation of $\text{CoCHOH}=\text{C}=\text{O}^+$, while in $\text{Co}(\text{CO})_2^+$ rearrangement to eliminate 2CO's and H_2O is the only reaction pathway.

$\text{Co}(\text{CO})_n\text{NO}^+$ ions react by ligand substitution reactions with loss of up to 2 CO's.

In this compound, two new reactions are observed for CoCO^+ that were not observed for Co^+ : elimination of acetic acid and the elimination of CH_2 :. The former reaction involves insertion of CoCO^+ into the $\text{CH}_2\text{OH}-\text{CH}_2\text{COOH}$ bond, where the CO is adjacent to the CH_2OH group, then a β -H atom shift to give a $(\text{CHOH}=\text{C})\text{Co}^+$ (CH_3COOH) complex from which elimination of the acid occurs.

Table 37. The reactions of cobalt containing ions with
2-hydroxyacetic acid ($M = CH_2OHCOOH$).

$Co^+ + M \longrightarrow CoCHOH=C=O^+ + H_2O$	(100%)
$CoCO^+ + M \longrightarrow CoM^+ + CO$	(98%)
$\longrightarrow CoCHOH=C=O^+ + H_2O + CO$	(2%)
$Co(CO)_2^+ + M \longrightarrow CoCHOH=C=O^+ + H_2O + 2CO$	(100%)
$CoNO^+ + M \longrightarrow$ No Reaction	
$CoCONO^+ + M \longrightarrow CoNOM^+ + CO$	(100%)
$Co(CO)_2NO^+ + M \longrightarrow CoNOM^+ + 2CO$	(100%)
$Co(CO)_3NO^+ + M \longrightarrow CoCONOM^+ + 2CO$	(100%)

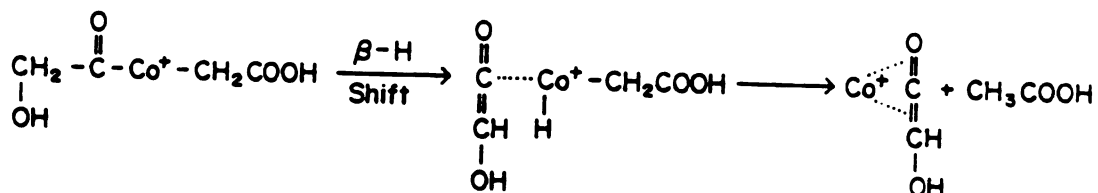
Table 38. The reactions of cobalt containing ions with 3-hydroxypropanoic acid ($M = CH_2OHCH_2COOH$).

$Co^+ + M \longrightarrow$	$CoH_2O^+ + CH_2=CHOOH /$ $CoH_2O^+ + CH_2OHCH=C=O$	(25%)
\longrightarrow	$CoCH_2=CHCOOH^+ + H_2O /$ $CoCH_2OHCH=C=O^+ + H_2O$	(14%)
\longrightarrow	$CoCH_2CHOH^+ + HCOOH$	(51%)
\longrightarrow	$CoHCOOH^+ + C_2H_3OH$	(10%)
$CoCO^+ + M \longrightarrow$	$CoM^+ + CO$	(9%)
\longrightarrow	$CoH_2O^+ + CH_2CHCOOH + CO /$ $CoH_2O^+ + CH_2OHCHCO + CO$	(62%)
\longrightarrow	$CoCOH_2O^+ + CH_2CHCOOH /$ $CoCOH_2O^+ + CH_2OHCHCO$	(3%)
\longrightarrow	$CoCH_2CHCOOH^+ + H_2O + CO /$ $CoCH_2OHCHCO^+ + H_2O + CO$	(19%)
\longrightarrow	$CoCOCH_2O^+ + CH_3COOH$	(5%)
\longrightarrow	$CoCOCH_2OHCOOH^+ + CH_2$	(2%)
$Co(CO)_2^+ + M \longrightarrow$	$CoM^+ + 2CO$	(16%)
\longrightarrow	$CoCOH_2O^+ + CH_2CHCOOH + CO /$ $CoCOH_2O^+ + CH_2OHCHCO + CO$	(81%)
\longrightarrow	$Co(CO)_2CH_2=C(OH)_2^+ + CH_2O$	(3%)
$CoNO^+ + M \longrightarrow$	No Reaction	

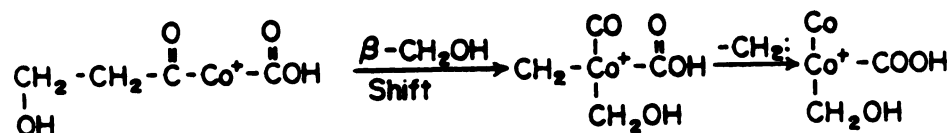
Table 38 Continues.

Table 38 Continued.

$\text{CoCONO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + \text{CO}$	(8%)
\longrightarrow	$\text{CoNOCH}_2\text{CHCOOH}^+ + \text{H}_2\text{O} + \text{CO}/$ $\text{CoNOCH}_2\text{OHCHCO}^+ + \text{H}_2\text{O} + \text{CO}$	(15%)
\longrightarrow	$\text{CoNOH}_2\text{O}^+ + \text{CH}_2\text{CHCOOH} + \text{CO}/$ $\text{CoNOH}_2\text{O}^+ + \text{CH}_2\text{OHCHCO} + \text{CO}$	(77%)
$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoNOM}^+ + 2\text{CO}$	(20%)
\longrightarrow	$\text{CoNOCH}_2\text{CHCOOH}^+ + \text{H}_2\text{O} + 2\text{CO}/$ $\text{CoNOCH}_2\text{OHCHCO}^+ + \text{H}_2\text{O} + 2\text{CO}$	(16%)
\longrightarrow	$\text{CoNOH}_2\text{O}^+ + \text{CH}_2\text{CHCOOH} + 2\text{CO}/$ $\text{CoNOH}_2\text{O}^+ + \text{CH}_2\text{OHCHCO} + 2\text{CO}$	(64%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M} \longrightarrow$	$\text{CoCONOH}_2\text{O}^+ + \text{CH}_2\text{CHCOOH} + 2\text{CO}/$ $\text{CoCONOH}_2\text{O}^+ + \text{CH}_2\text{OHCHCO} + 2\text{CO}$	(42%)
\longrightarrow	$\text{Co}(\text{CO})_2\text{NOH}_2\text{O}^+ + \text{CH}_2\text{CHCOOH} + \text{CO}/$ $\text{Co}(\text{CO})_2\text{NOH}_2\text{O}^+ + \text{CH}_2\text{OHCHCO} + \text{CO}$	(58%)



The elimination of $\text{CH}_2:$ occurs via CoCO^+ insertion into the $\text{CH}_2\text{-COOH}$ bond followed by a $\beta\text{-CH}_2\text{OH}$ shift to the metal. As observed in the 3-chloropropanoic acid, the $\text{CH}_2\text{X-CH}_2\text{COOH}$ bond is weakened, making the likelihood of the CH_2OH shift feasible.



As was observed in the unsubstituted acids, the elimination of $\text{CH}_2:$ is a minor product. This reaction is also observed in Co(CO)_2^+ .

The $\text{Co(CO)}_n\text{NO}^+$ ions also react to give $\text{Co(CO)}_n'\text{NO(H}_2\text{)}^+$ or $\text{Co(CO)}_n'\text{NO(M-H}_2\text{O)}^+$ products. As discussed in the chemistry of Co^+ , attack at either OH group can occur

readily making an absolute structure assignment difficult. Most likely both structures are present.

4. The Mercapto-Acids

In Tables 39 and 40 are the reactions of each metal containing ion with the mercaptoacids. Also in these tables are the branching ratios.

With one small exception, CoCO^+ reacts with 2-mercaptoacetic acid the same as Co^+ does. Co^+ was observed to react with this acid to lose HOSH ; CoCO^+ loses either just the S atom or the S atom and a CO as SCO. The mechanism for this reaction involves the formation of the five membered ring intermediate that was proposed for the COH elimination, except the C-S bond is broken in the reaction. After the formation of the ring intermediate and H atom shift to give $\text{CoCO}(\text{S})(\text{CH}_2=\text{C}(\text{OH})_2)^+$, competitive ligand loss occurs via the elimination of S or SCO. When Co^+ reacted by the same intermediate, it loses CoH.

$\text{Co}(\text{CO})_2^+$ and CoCONO^+ react to give similar products as above. In all CoL_n^+ ions, except for CoNO^+ , reactions at the CO-OH bond occurs with the retention of H_2O by the metal containing ion.

CoCO^+ again reacts similarly to Co^+ with this acid. CoCO^+ reacts at both functional groups and also reacts via the cyclic intermediate. The product ion ($m/z = 133$) formed by the latter pathway could also be $\text{CoCO}(\text{HCOOH})^+$

Table 39. The reactions of cobalt containing ions with 2-mercaptoacetic acid ($M = CH_2SHCOOH$).

$Co^+ + M \longrightarrow$	$CoH_2O^+ + CHSH=C=O$	(35%)
\longrightarrow	$CoCHSH=C=O^+ + H_2O$	(32%)
\longrightarrow	$(M-H)^+ + CoH$	(11%)
\longrightarrow	$CoCH_2=C=O^+ + HOSH$	(22%)
$CoCH^+ + M \longrightarrow$	$CoM^+ + CO$	(25%)
\longrightarrow	$CoH_2O^+ + CHSHCO + CO$	(12%)
\longrightarrow	$CoCHSHCO^+ + H_2O + CO$	(4%)
\longrightarrow	$CoCH_2=C(OH)_2^+ + S + CO$	(18%)
\longrightarrow	$CoCOCH_2=C(OH)_2^+ + S$	(34%)
\longrightarrow	$(M-H)^+ + CoCOH$	(7%)
$Co(CO)_2^+ + M \longrightarrow$	$CoCOH_2O^+ + CHSHCO + CO$	(25%)
\longrightarrow	$CoCOCH_3COOH + S + CO$	(72%)
\longrightarrow	$CoCH_3COOH + S + 2CO$	(3%)
$CoNO^+ + M \longrightarrow$	No Reaction	
$CoCONO^+ + M \longrightarrow$	$CoNOH_2O^+ + CHSH=C=O + CO$	(10%)
\longrightarrow	$CoNOCH_3COOH + S + CO$	(90%)

Table 39 Continues.

Table 39 Continued.

$\text{Co}(\text{CO})_2\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 2\text{CO}$	(24%)
	$\longrightarrow \text{CoCONOH}_2\text{O}^+ + \text{CHSHCO} + \text{CO}$	(63%)
	$\longrightarrow \text{CoNOH}_2\text{O}^+ + \text{CHSHCO} + 2\text{CO}$	(13%)
$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 3\text{CO}$	(12%)
	$\longrightarrow \text{CoNOH}_2\text{O}^+ + \text{CHSHCO} + 3\text{CO}$	(22%)
	$\longrightarrow \text{CoCONOH}_2\text{O}^+ + \text{CHSHCO} + 2\text{CO}$	(66%)

Table 40. The reactions of cobalt containing ions with 2-mercaptopropanoic acid ($M = CH_3CHSHCOOH$).

$Co^+ + M \longrightarrow$	$CoH_2O^+ + CH_3CSH=C=O$	(21%)
\longrightarrow	$CoHCOOH^+ + CH_2CHSH$	(41%)
\longrightarrow	$Co(M-H_2S)^+ + H_2S$	(38%)
$CoCO^+ + M \longrightarrow$	$CoM^+ + CO$	(5%)
\longrightarrow	$Co(M-H_2S)^+ + H_2S + CO$	(29%)
\longrightarrow	$CoCO(HCOOH)^+ + C_2H_3SH$	(20%)
	$CoCH_3CH=C(OH)_2^+ + S + CO$	
\longrightarrow	$CoCOCH_3CH=C(OH)_2^+ + S$	(23%)
\longrightarrow	$CoCOH_2O^+ + CH_3CSHCO$	(15%)
\longrightarrow	$CoH_2O^+ + CH_3CSHCO + CO$	(8%)
$Co(CO)_2^+ + M \longrightarrow$	$CoM^+ + 2CO$	(14%)
\longrightarrow	$CoCOM^+ + CO$	(24%)
\longrightarrow	$CoCOH_2O^+ + CH_3CSHCO + CO$	(38%)
\longrightarrow	$CoCOCH_3CH_2COOH + S + CO$	(24%)
$CoNO^+ + M \longrightarrow$	$CoNOCH_3CSH=C=O^+ + H_2O$	(100%)
$CoCONO^+ + M \longrightarrow$	$CoNOM^+ + CO$	(47%)
\longrightarrow	$CoNOCH_3CH_2COOH + S + CO$	(53%)
$Co(CO)_2NO^+ + M \longrightarrow$	$CoNOM^+ + 2CO$	(64%)
\longrightarrow	$CoNOCH_3CH_2COOH + S + 2CO$	(36%)

Table 40 Continues.

Table 40 Continued.

$\text{Co}(\text{CO})_3\text{NO}^+ + \text{M}$	$\longrightarrow \text{CoNOM}^+ + 3\text{CO}$	(45%)
	$\longrightarrow \text{CoCONOM}^+ + 2\text{CO}$	(55%)

formed by insertion of the metal into the C-COOH bond and then a β -H atom shift process.

CHAPTER 10

SUMMARY AND CONCLUSIONS

The chemistry of alkyl thiols with Co^+ is similar to that observed with alkyl halides and alcohols. Primarily, Co^+ inserts into the C-SH bond followed by a β -H atom shift to give a $(\text{H}_2\text{S})\text{Co}^+(\text{olefin})$ intermediate. This intermediate then undergoes competitive ligand loss according to the metal-ligand affinities.

In several thiols insertion of Co^+ into C-C bonds followed by β -H atom shift may occur to yield smaller alkenes and thiols. In 1-butanethiol and 2-butanethiol, insertion by Co^+ into C-H bonds with the elimination of H_2 or H_2 and H_2S to give a $\text{Co}(\text{butadiene})^+$ complex may also occur.

The reactions of CoCO^+ and CoCONO^+ resemble the chemistry of Co^+ with thiols with one exception. In 2-propanethiol, CoCO^+ and CoCONO^+ react via CoCO^+ insertion into a C-C bond and eventually form $\text{Co}(\text{thioketene})^+$. Co^+ alone does not react with 2-propanethiol to give the thioketene.

The reactions of the other CoL_n^+ ions with the thiols are dominated by ligand substitution reactions.

The chemistry of Co^+ with butanone is dominated by insertion of the metal ion into either the $\text{CH}_3\text{-CO}$ or $\text{C}_2\text{H}_5\text{-CO}$ bond. From the appropriate intermediate either a $\beta\text{-H}$ atom shift can occur or an alkyl shift onto the metal center occurs.

The CoL_n^+ ions react primarily via ligand substitution. "Decomposition" reactions of these ions with butanone follow metal ion insertion into the $\text{C}_2\text{H}_5\text{-CO}$ bond, which is the weakest bond in this compound.

Co^+ and CoL_n^+ ions react analogously with 3-butenone as they did with butanone.

The chemistry of Co^+ with unsubstituted carboxylic acids involves initial metal ion insertion into either the C-CO bond or the CO-OH bond with the latter being the more favored site. After insertion into the C-CO bond a $\beta\text{-H}$ atom shift occurs followed by elimination of a ligand. When insertion into the CO-OH bond occurs either a $\beta\text{-H}$ atom shift occurs or an alkyl shift occurs to yield a $\text{Co}(\text{CO})(\text{alcohol})^+$ complex which then eliminates a ligand or undergoes reactions typical of the alcohol to give $\text{CoCO}(\text{H}_2\text{O})(\text{olefin})^+$ which then loses various ligands.

$\text{Co}(\text{CO})_x^+$ and $\text{Co}(\text{CO})_y\text{NO}^+$ ions react with carboxylic acids similarly to the reactions of these ions with monofunctional compounds. CoNO^+ shows a variation of its chemistry when the alkyl chain increases in length. In acetic and propanoic acids, after insertion into the Co-OH bond and a $\beta\text{-H}$ shift to give $\text{CoNO}(\text{H}_2\text{O})(\text{ketene})^+$,

the water is retained by the metal center. In the reaction of CoNO^+ with butanoic acid elimination of H_2O occurs. After the formation of the $\text{CoNOH}_2\text{O}(\text{ketene})^+$ complex there lies the possibility for the metal center to insert into a C-C bond of the ketene.

Allylic compounds were the first bifunctional molecules to be studied. The reactions of Co^+ with these compounds were typical of the X-functional group with the exception of allyl amine. Normally, Co^+ will not react with amines via insertion into the C-N bond to give either $\text{Co}(\text{olefin})^+$ or CoNH_3^+ . This is due to the weak Co^+-NH_2 bond formed. However in allyl amine, the weak Co^+-NH_2 bond is overshadowed by the very strong $\text{Co}^+-\text{C}_3\text{H}_5$ interaction which then allows a β -H atom to shift with the elimination of NH_3 .

The various CoL_n^+ ions react differently than one would expect. As the number of ligands increases, new reactions due to ligand participation occur. For example, $\text{Co}(\text{CO})_2\text{NO}^+$ typically reacts via ligand substitution, but with allyl amine, retention of NH_3 (as H and NH_2) and loss of allene is observed.

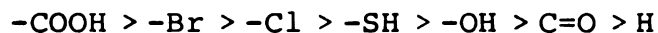
With substituted ethanol, Co^+ shows a preference for the halogen functional group over the OH. Also formation of a five-membered ring intermediate also occurs, which eliminates C_2H_4 . For 2-bromoethanol, the elimination of HOBr is also observed as well as numerous reactions involving radical formation.

The CoL_n^+ ions also show several cases of ligand participation in the reaction especially in the chemistry of $\text{Co}(\text{CO})_{2,3}\text{NO}^+$ with 2-bromoethanol.

The ability to predict the reactions of Co^+ with bifunctional compounds can vary from 0% to 100% accuracy depending upon the compound. In each case more reactions were predicted than actually observed. This is because the reactions were predicted based upon the known chemistry of each functional group and not on metal-ligand affinities. In cases where 100% of the reactions were not predicted new reactions involving some type of interaction between the metal and both groups explained the observed reactions.

The CoL_n^+ ions for the most part show similar chemistry to the bare metal ion, in a few cases where ligand participation is a factor.

The following trend for site of attack by Co^+ can be suggested:



This trend was derived from the observed reactions and branching ratios for Co^+ with the substituted ketones and carboxylic acids. In Table 27 are the reactions of Co^+ with the substituted butanones. Examining the branching ratios for reactions due to the ketone functional group and the X group, it is observed that the X-group contributes

more to the total reaction pathway. Also from this table, the Br functional group is preferred more than the chloride and hydroxy groups. Also the Cl is preferred over the OH.

Placement of the -SH functional group was based upon the amount of H_2S formed from 2-mercaptopropanoic acid compared to the amount of H_2O formed from 3-hydroxypropanoic acid. This may not be a valid method of comparison due to obvious structural differences, but using these results in conjunction with the fact that the C-SH bond is weaker than the C-OH bond one can assume that the C-SH bond would be more reactive.

The acid functional group was placed as being the most reactive site by Co^+ . There could be arguments against this placement. Looking at Tables 28-30 there is a possibility of placing this group below the halides and alcohol from the branching ratios due to cases where the X-group appears to be more reactive. But in more cases the Co^+ prefers to react at the COOH group.

The hydrogen group was placed at the bottom of the list because very few reactions were observed due to Co^+ insertion into C-H, O-H and S-H bonds.

In 1974, Michnowicz and Munson [51] observed a similar trend in the methane CIMS study of steroidal ketones, with one exception



The C=O functional group is more reactive than the halides and alcohol. No thiol substituted steroids were studied. Munson's study reflects the difference in the basicity of the various functional groups. This study not only depends upon the ability of the metal to complex with the functional group but also the metal's ability to insert into various bonds in the molecule.

APPENDICES

APPENDIX A

APPENDIX A

Table 41. Pertinent Proton Affinities.

<u>Compound</u>	<u>PA (kcal/mole)</u>	<u>Reference</u>
H ₂	101	52
CO	139	53
CH ₄	128	54
C ₂ H ₂	152	55
C ₂ H ₄	160	55
C ₃ H ₆	179	56, 57
n-C ₄ H ₈	183	58
i-C ₄ H ₈	193	56, 57
HCl	141 ± 3	54
HBr	140 ± 3	54
CH ₃ Cl	160	59
CH ₃ Br	163	59
NH ₃	205	60
H ₂ O	165 ± 3	61
CH ₃ OH	182	61
C ₂ H ₅ OH	190.3	62
H ₂ S	170 ± 3	61
CH ₃ SH	185	61
HCOOH	178	63
CH ₃ COOH	188	64
CH ₃ CH ₂ COOH	189.5	65
CH ₂ ClCOOH	182.4	65
CH ₃ CHO	185	61
CH ₂ CO	201 ± 2	66

APPENDIX B

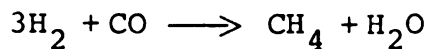
APPENDIX B

WATER GAS SHIFT REACTION

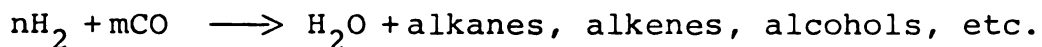
In this appendix is described a short project attempted in Fall 1981 — the investigation of the water gas shift reaction using ICR.

A. Introduction

Whenever a carboneous deposit, such as coal or oil, is found, a mixture of CO, CO₂, H₂O and H₂, known as water gas or synthesis gas, is also found. This water gas is believed to be a precursor of these carboneous materials, which are formed through the reactions of hydrogen or water with carbon monoxide according to the following:



and



The second reaction is the Fischer-Tropsch reaction.

Water gas, as it occurs naturally, contains between one and two moles of H_2 per mole of CO . In order for production of organic compounds to occur, the H_2 content must be increased. This is effected through the water gas shift reaction (WGSR):

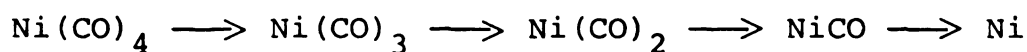


A major goal of catalysis research is to develop catalysts that would increase the hydrocarbon or H_2 yield from the last two reactions. This work encompasses the pre-World War II experiments by Fischer and others [67] in the search for heterogeneous catalysts to produce hydrocarbons, as well as more recent work by Darenbourg and others [68-75] using metal carbonyls as homogeneous catalysts for the water gas shift reaction. Not only yields of hydrocarbons and hydrogen were investigated, but also the mechanisms involved. Among the mechanisms suggested, the intermediates most often proposed include metal carbides, formaldehyde-metal complexes ($M(CH_2O)$), and η^2 -CO bonding complex [75]. The proposed intermediates are specific for each metal and experimental methods used.

One of the more recent and exotic approaches to study CO reduction has been through temperature programmed decomposition experiments (TPDE) [73]. The most efficient

homogeneous catalysts have been polynuclear carbonyls. This may be because these multinuclear centers are required to activate the carbon monoxide substrate. An alternative concept is that mononuclear carbonyls (which are stable under the reaction conditions of high temperature and pressure) are catalytically active.

In TPDE, metal carbonyls are thermally decomposed on alumina or silica to give subcarbonyl species, i.e.



Among compounds tested were $\text{Mn}_2(\text{CO})_{10}$, $\text{Ru}_3(\text{CO})_{12}$, Cr(CO)_6 , Fe(CO)_5 and Ni(CO)_4 . The activities of these compounds were measured as a function of the moles of CH_4 produced per mole of metal. The results indicate that polynuclear carbonyls are more reactive than the mononuclear.

As different investigators develop new techniques and use different and exotic compounds for the WGS, new mechanisms arise. Some examples follow.

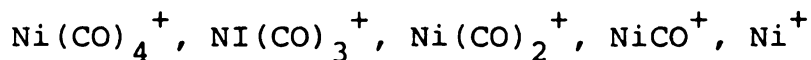
Wong and Labinger [74], using $(\eta^5\text{-C}_5\text{H}_5)\text{NbH}_3$ and Cr(CO)_6 in the presence of H_2 , observed selective formation of C_2 hydrocarbons, mainly ethane. By using D_2 , and intermediates of methylene, $:\text{CH}_2$ ($:\text{CD}_2$), is shown to be formed.

Casey [76] using $\text{C}_5\text{H}_5\text{Re}(\text{NO})(\text{CO})_2^+$ and BH_4^- proposed a mechanism using a $-\text{CH}_3$ complex, $\text{C}_5\text{H}_5\text{Re}(\text{NO})(\text{CO})(\text{CH}_3)$. Other work on other compounds suggest intermediates such as a $\eta\text{-CO}$ conditioning mode.

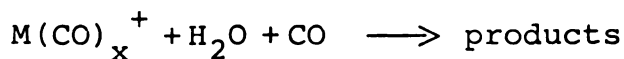
B. Project Description

Most of the work done on the WGSR has been done on a pressure range from 0.9 atm up to 1000 atm, and a wide range of temperatures as well (100-400°C). Under these conditions it is difficult to isolate intermediates and only final products are observed. For example, the TPDE subcarbonyl species $\text{Ni}(\text{CO})_3$, $\text{Ni}(\text{CO})_2$ and NiCO are adsorbed on alumina and cannot be isolated separately. Also one may not be sure if one species or another is more reactive.

With ICR some of these problems can be solved. For example, if we take $\text{Ni}(\text{CO})_4$ at low pressure, the following positive ions are formed:



The reactions of $\text{Ni}(\text{CO})_4^+$ will parallel experiments with mononuclear carbonyls, while the other ions will parallel TPDE studies of subcarbonyl species. The intended work center around the reactions



If the reaction

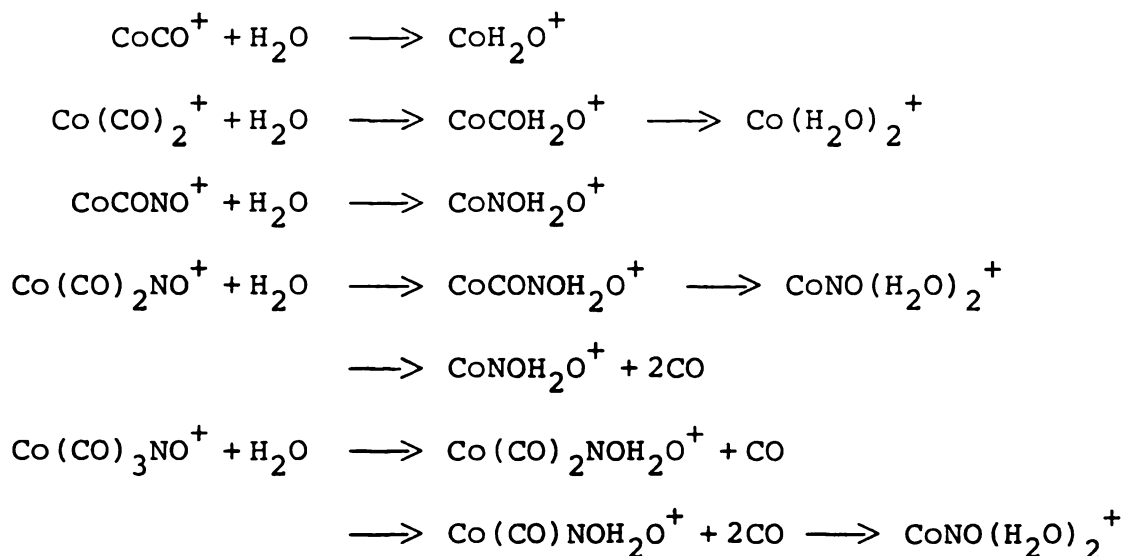


it may be evidence for a formaldehyde intermediate. To test this, using formaldehyde we can see if $M(CO)_2^+$ reacts in the same way.

C. Results and Discussion

The majority of work done on the water gas shift reaction involved the ions derived from $Co(CO)_3NO$. None of the ions reacted with H_2 at any pressure or ratio of metal: H_2 . This is due to the poor nature of H_2 as a ligand ($PA(H_2) = 101$ kcal/mole). If a complex were to form between $Co(CO)_x^+$ or $Co(CO)_xNO^+$ with H_2 , the poorest ligand would be lost. Most likely there would not be any chance for the H-H bond to cleave enabling the H atoms to bond to the metal or CO.

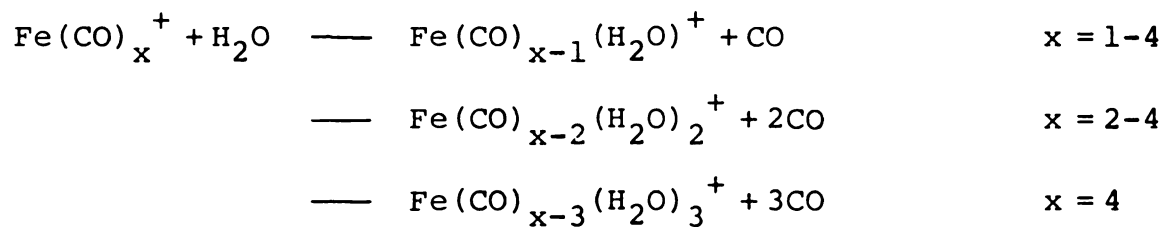
In investigating the chemistry of these ions with the other component of the WGS, (H_2O), ligand substitution reactions only occurred.



As can be seen here the components of the WGSR are placed on the metal, that is, CO and H₂O are together on the metal ion. The exact form (CO/H₂O, CO₂/H₂ or HCOOH) could not be determined. In an attempt to elucidate the product ion structure, I would have liked to have done further ligand displacement studies. If a third gas, with a higher metal-ligand affinity than CO and H₂O, was admitted to the ICR, displacement of CO, H₂O or both should occur. By varying the proton affinity of this third gas sample, the determination of the product ion structure might have been possible.

This ligand displacement study was not performed because at that time the ICR was equipped with only two inlet lines.

Similar reactions with H₂O and the ions of Fe(CO)₅ were observed. The ligand displacement reactions were identical to those observed by Foster and Beauchamp [77].



Again ligand displacement studies were desired but could not be performed.

Our initial goal of this project was to see if any small hydrocarbons or aldehydes or alcohols could be formed under the conditions in the ICR. In all the studies performed no evidence for these reactions was observed and it was decided to shelf this study for one that looked more promising.

APPENDIX C

APPENDIX C

USING THE ZX 81 TO CONTROL TRAPPED ICR EXPERIMENTS

Experiments in this dissertation were performed on an ICR in the drift mode. Drift mode is the experimental set-up in which the ions start moving from the source region of the ICR cell to the analyzer region as soon as they are formed. This set-up allows for a few collisions before the ions are detected.

An alternative method of using the ICR is in the trapped mode. The ions are held in the source region for a finite time and then allowed to drift to the analyzer for detection. Since the ions are held in the source for longer periods, more collisions occur which result in greater conversion of the reactants to product ions [78].

The ICR spectrometer in use at Michigan State University is capable of being used in either mode. In the drift mode, one trapping plate in the source has a square wave signal on it to modulate the experiment. For example, if one is analyzing positive ions, one of the two source trapping plates would always be at a positive potential, the other trapping plate would be at that

which can be opened and closed using POKE statements. To close a relay, the user POKEs in a number corresponding to the binary equivalent of the relay to be closed into memory location 32766. For example, to close the rightmost relay one would enter POKE 32766,1; to close the next relay enter POKE 32766,2. If the user wants to close more than one relay, he/she simply adds the two numbers. For example, POKE 32766,255 will close all the relays. Each relay has a LED associated with it to indicate if it is closed (LED on). The relays are rated at 0.75 amps max switch and 2 amps max carry. They are rated to carry a maximum of 200 VDC. A card edge connector is used to connect the ICR voltages to the relays.

The program contains a BASIC routine which allows the user to enter the pulsing sequence that he/she desires. In an early version of this program, the user has to enter which relays to be closed and a parameter to determine the pulse width. This required the user to look up in a table the appropriate factor. The shortest usable pulse was 1.52 msec, the longest pulse that could be used in one step was 400 msec. If pulses longer than 400 msec were desired, the user entered a multiple request for that relay. As pulses became longer, limitations due to resolution of the programming arose. By this is meant, if a pulse of 202 msec was desired that user

could not POKE in the appropriate value directly, a number of 178 save a pulse width of 200 msec and 179 save a pulse width of 205 msec, therefore the user had to make at least two relay requests to get a pulse width of 202 msec (number 127 and 128 gives pulse widths of 100 and 102 msec, respectively). Therefore, before using this program the user had to calculate each relay and for how long it was to be on.

A modification of the BASIC program needed to be done. A second program made an assumption that the minimal pulse width was 5 msec and that longer pulses were multiples of this. This allowed for 200 individual on-off transitions to occur. (The earlier version allowed 255 transitions to occur.) The BASIC routine prompted the user when each relay was to be closed and opened in the one second time span, multiple closings and openings are permitted. The computer then calculates the sequence of which relays are closed at each 5 msec interval and stores them in memory. After calculating the sequence the computer then inquires if any errors were made in the entry of the sequence. If there were, the memory is cleared and the sequence is re-entered. If no errors were made the BASIC routine yield control to the machine language user routine.

The machine language routine has three parts to it. The first is portion loads the starting memory location of the pulse sequence into register HL, the contents of this

location is then loaded into register A and stored in memory location 40BB. The A register is decremented by 1 and compared to register B (set equal to zero). If the result is equal to zero the last item in the sequence has been reached and the machine language routine jumps to START which loads the starting memory location into HL.

If the last item in the sequence was not reached, the second portion of the routine is encountered. This portion loads the RELAY REGISTER with the relay to be closed. This is the machine language equivalent of a POKE statement. The next item in the list, the pulse width parameter, is then stored in registers B and C. A nested loop then decreases each register causing the selected relay(s) to be closed for 5 msec (if the second BASIC program was used).

After the nested loop are executed the machine code enters the user routine ending subroutine. This subroutine calls a ROM subroutine that looks to see if any key was struck [79]. If a key was struck, the program returns to the BASIC program and prompts the user if the same or a new sequence is to be used or if the user wishes to stop. If no key was struck, the machine language routine then jumps to 4089h and loads the next item from the list and continues as before.

One item to note is the pulse width is not just determined by the nested loop but also by the number of operations done between the POKE statement. Also the

second BASIC program allows 200 5 msec pulse width intervals in one second; if the minimal pulse width is to be longer a change in the pulse width parameter in the BASIC routine has to be performed. (Figure 5).

These programs were tested using a 5 volt power supply as the load on the relays and the output was monitored on an oscilloscope. These programs were never used in an actual experiment to date.

address (hexadecimal)	MC	Label	Op
4082	213075	START	LD HL,LIST
4085	7E		LD A,(HL)
4086	32BB40		LD COUNT, A
4089	3ABB\$0	LOOP	LD A,COUNT
408C	0600		LD B,0
408E	3D		DEC A
408F	32BB40		LD COUNT, A
4092	B8		CP B
4093	2BED		JR Z, START
4095	23		INC HL
4096	7E		LD A, (HL)
4097	32FE7F		LD RR,A
409A	23		INC HL
409B	3E00		LD A,0
409D	46		LD B, (HL)
409E	4E	2\$	LD C, (HL)
409F	0D	1\$	DEC C
40A0	B9		CP C
40A1	20FC		JR NZ 1\$
40A3	05		DEC B
40A4	B8		CP B
40A5	20F7		JR NZ 2\$
40A7	E5		PUSH HL
40AB	CEBB02		CALL KSCAN
40AB	44		LD B,H
40AC	4D		LD C,L
40AD	51		LD D,C
40AE	E1		POP HL
40AF	14		INC D
40B0	3E00		LD A,0
40B2	CA8940		JP Z, LOOP
40B4	C9	END	RET

The BASIC controlling program for the modified pulsing sequence is given below.

```
1 REM "RELAYS"
2 REM MACHINE LANGUAGE ROUTINE- NON PRINTABLE
1000 DIM R(201)
1010 DIM N(8)
1020 DIM F(F)
1030 FOR I=1 TO 200
1040 LET R(I)=0
1050 NEXT I
1060 FOR R=1 TO 8
1065 CLS
1070 PRINT "DOES RELAY ";R;"COME ON IN THIS EXPERIMENT?(Y
      OR N)"
1080 INPUT A$
1090 IF A$(1)="N" THEN GOTOT 1270
1100 PRINT "INPUT AT WHAT TIME DOES RELAY ";R;"COME ON
      AND GOES OFF";
1110 INPUT N(R)
1120 INPUT F(R)
1130 PRINT N(R),F(R)
1140 LET J=N(R)/5
1150 LET K=N(R)/5
1160 IF R=1 THEN LET RF=1
1170 IF R=2 THEN LET RF=2
1180 IF R=3 THEN LET RF=4
1190 IF R=4 THEN LET RF=8
1200 IF R=5 THEN LET RF=16
1202 IF R=6 THEN LET RF=32
1204 IF R=7 THEN LET RF=64
1206 IF R=8 THEN LET RF=128
1210 FOR L=J+1 TO K
1220 LET R(L)=R(L)+RF
1230 NEXT L
1240 PRINT "DOES RELAY ";R;" COME ON AGAIN IN THE SAME
      SECOND?(Y OR N)"
1250 INPUT A$
1260 IF A$(1)="Y" THEN GOTO 1100
1270 NEXT R
1275 CLS
1280 LET I=30000
1290 POKE I,201
1300 FOR M=1 TO 200
1310 LET I=I+1
1320 POKE I,R(M)
1340 LET I=I+1
1350 POKE I,27
1360 NEXT M
1370 CLS
```

```
1380 PRINT " TO STOP PROGRAM NOW INPUT ""S"". TO STOP  
      PROGRAM ANY OTHER TIME HIT ANY KEY. INPUT ANY LETTER."  
1390 INPUT A$  
1400 IF A$(1)="S" THEN STOP  
1410 FOR D=1 TO 200  
1420 NEXT D  
1430 RAND USR 16514  
1440 PRINT " WELCOME BACK. DO YOU WANT THE SAME SEQUENCE,  
      NEW SEQUENCE OR QUIT? (INPUT S OR N OR Q)"  
1450 INPUT A$  
1460 IF A$(1)="S" THEN GOTO 1410  
1470 IF A$(1)="N" THEN GOTO 1030  
1480 STOP
```

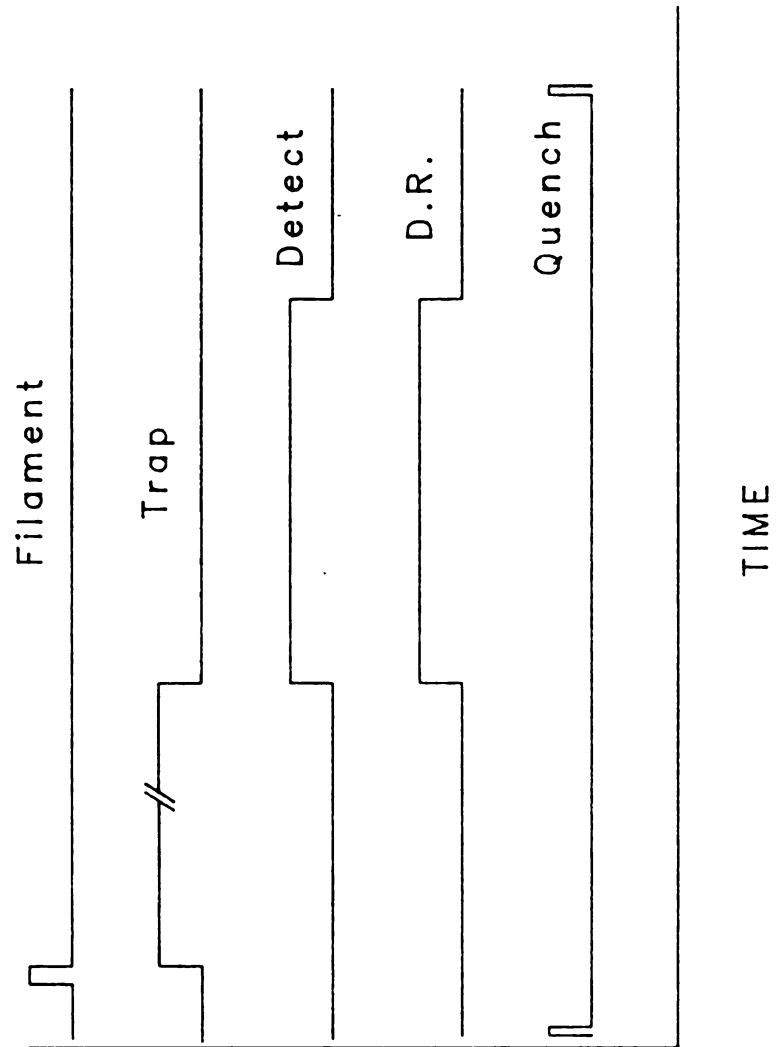


Figure 5. Timing Diagram for Pulsed ICR.

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