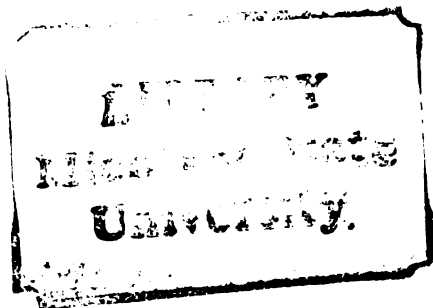
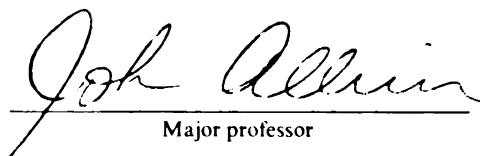




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GAS PHASE TRANSITION METAL ION CHEMISTRY

By

Sunkwei Huang

A DISSERTATION

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

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1983

ABSTRACT

GAS PHASE TRANSITION METAL ION CHEMISTRY

By

Sunkwei Huang

Catalysis attracts tremendously broad interest and constitutes an important research field for chemists. Although there are a plethora of papers being published to probe the catalytic behavior of surfaces and homogeneous organometallic complexes, the behavior of a single metal center is usually not well understood due to the complications of ligand electronic effects (for the former) and solvent effects (for the latter).

Recently, Muetterties et al. have reported studies on metal clusters in an attempt to build a conceptual bridge between molecular and solid state chemistry. However, all of these fields have suffered from a lack of sufficient thermochemical and structural information and are still inevitably somewhat speculative in nature. Gas phase transition metal ion/molecule reactions help to provide answers to the following questions:

1. How do metal centers react with molecules in the absence of solvent molecules?
2. What factors control these reactions?
3. How can we apply these answers to obtain a better understanding and control of macroscopic synthetic systems?

In this dissertation, the chemistries of ions such as Fe^+ , Cr^+ , and Ni^+ (containing multiple numbers of CO ligands) with multifunctional organic molecules are reported. Mechanistic effects, ligand effects, the differences in chemistries of these metal ions and their reaction mechanisms with ethers and polyethers will be discussed. Also, a unique "double insertion, double β -H shift" mechanism is proposed to explain the results of these metal ion reactions with cyclic polyethers.

Since the reaction products we have observed in this ICR study are mass spectrometric peaks, the assignment of ion structures sometimes ambiguous, although some techniques such as double resonance, CID, and the use of labelled compounds can provide some useful information. Ab initio calculations can provide much information such as energy levels of various electronic states, orbital occupancies, etc. The structure of CrCH_2^+ is given as an example to elucidate the use of this technique.

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I also want to thank my parents and parents-in-law and all the members in our two families for giving me confidence and keeping the families in good shape so that I didn't need to worry about my father or father-in-law's sickness.

Thank you, Dr. Allison. For four years, I have learned very much from you. I really appreciate your sincere direction of my research work and also for giving me the courage to be a good scientist and teacher. I will always remember that you were the preceptor who put me in the right track for my later career and who helped me in many aspects....

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THE TECHNIQUE

A. THE TECHNIQUE - ION CYCLOTRON RESONANCE SPECTROSCOPY

1. Introduction

Ion Cyclotron Resonance (ICR) Spectrometry is a type of mass spectrometry especially designed for the study of ion-molecule reactions in the gas phase. ICR experiments provide a variety of chemical information such as acidity, basicity, heats of information, bond strengths, proton affinities and all types of information related to the chemical reaction¹.

There are quite a few reviews available on this technique¹⁻⁹. ICR is based on the dynamics of charged particles in electric and magnetic fields⁸. The detection system consists of a marginal oscillator (M.O)^{10,11} or frequency sweep detector^{12,13} with phase sensitive detection¹⁴. The basic principle of ICR will be discussed.

2. The ICR Experiment

A block diagram of an ICR spectrometer is shown in Figure 1. Figure 2 shows a detailed view of the three section ICR cell which is, in our laboratory, 0.88" x 0.88" x 6.25". The source is 2.00" long, analyzer region is 3.75" long and the collector is 0.50" long.

The cell is placed between the poles of an electromagnet. It is housed in a stainless steel vacuum chamber which can be evacuated to a pressure of 1.0×10^{-7} torr.

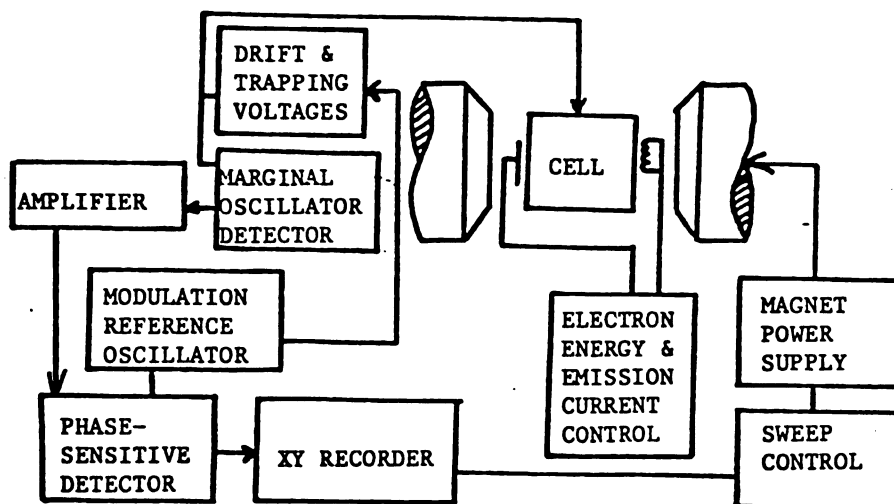


Figure 1.
Block Diagram Of ICR Spectrometer For
Single Resonance Experiment

The cell, situated in the magnetic field as shown in Figure 2, consists of an ion source, analyzer and collector. The electrons are emitted from a rhenium wire located outside of the cell by operating the electron energy and emission control as shown in Figure 1. Emitted electrons follow magnetic field lines, forming a collimated beam which crosses the cell are collected by a collector located on the opposite side of the cell, and are detected as emission current. The emission controller then regulates the emission current with a feedback circuit to provide a constant emission current. The electron current control can be used to adjust emission current (μ A) and electron energy (0 to -100 eV bias).

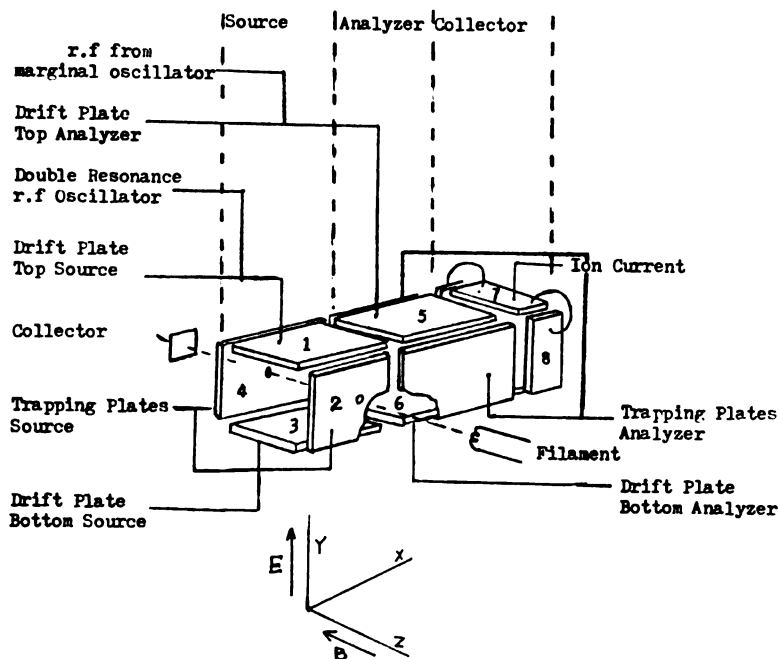


Figure 2.

The ICR Cell

Once ions are produced by electron impact, they will move circularly in a uniform magnetic field $\vec{B}$ with angular frequency of

$$\omega_c = \frac{eB}{mc} \quad (\text{radians/sec}) \quad (1)$$

where m is the mass of the ion and c is the speed of light.

Then, by applying a voltage E across the drift plates of the ICR, the ions will be "drifted" down to the analyzer section where the M.O. detector is set to one specific frequency (for instance 153 KHz) with a drift velocity (v_α) of

$$V_d = \frac{Ec}{B} \quad (2)$$

One can then scan the magnetic field to bring ions having different angular frequencies due to different masses according to equation (1) to be at resonance with the marginal oscillator. The ions can be detected as the power drop due to the power absorption from the LC resonant circuit of the M.O.^{10,11}.

Data in this dissertation were obtained under normal drift-mode conditions using trapping voltage modulation and phase sensitive detection (See Appendix A for detailed hardware description). The marginal oscillator detector is based on the design of Warnick, Anders and Sharp¹¹. In this technique, ions are produced in the source by an electron beam with 70 eV electrons. In the presence of a magnetic field, ions move in a circular orbit in the XY plane. To prevent ions from drifting to plates 2 and 4 in the Z direction, a trapping potential is applied to these plates ($V_{\text{trap}} > 0$ for positive ions, < 0 for negative ions), which creates a potential well near the center of the cell to trap the ions.

By applying a voltage difference E across the top and bottom plates which are called drift plates (#1,3,5,6), the ions experience an $\vec{E} \times \vec{B}$ force, drifting toward the analyzer where the top and bottom plates (5, 6) form the capacitive element of the tank circuit of the marginal oscillator

detector (See Appendix B). When ions move with a cyclotron frequency equal to the natural frequency of the tank circuit, they will absorb power from it and are detected. The S/N (signal to noise ratio) of the detector output is greatly enhanced by use of a lock-in amplifier¹⁴. The reference wave for the lock-in amplifier is provided by a function generator, at a frequency of 25 Hz. To effectively improve S/N, the signal output of the marginal oscillator must be modulated at this frequency. This is done by using the same 25 Hz square wave to modulate the signal out of the cell, which can be easily accomplished by modulating the voltage on one trapping plate (e.g. plate 4) as shown in Figure 3. This modulates the presence of ions to be detected in the cell. If plate 2 is (+), and plate 4 is modulating, when 4 is (+), cations are trapped and when 4 is (-), all ions are swept out of the cell. As a result, the rf level of the marginal oscillator varies at the modulating frequency, and forms a 25 Hz modulated signal output to be processed by the lock-in amplifier.

Usually, the marginal oscillator is operated at a frequency of $\simeq 153$ KHz ($\omega_{M.0}$) for convenience (see Appendix C). The magnetic field is varied (0-18 KG) so the cyclotron frequencies (ω_c) of all ions present also vary. When ω_c of an ion matches $\omega_{M.0}$, power is absorbed and the ion is detected.

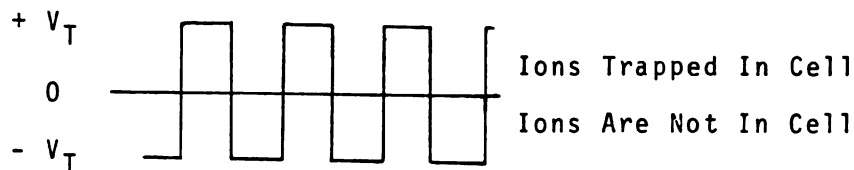


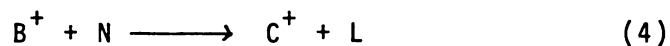
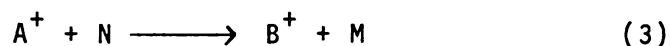
Figure 3

Modulation Of V_{Trapping} (frequency ≈ 25 Hz)

Figure 4 shows typical ICR spectra of $\text{Cr}(\text{CO})_6$, p-dioxane and a 1:1 mixture (in pressure) of $\text{Cr}(\text{CO})_6$ and p-dioxane.

At high pressures, e.g. 1×10^{-5} torr, a sufficient number of ion-neutral collisions occur to produce ion-molecule reaction products. To unambiguously identify reaction sequences, an ion cyclotron double resonance (CDR) experiment is performed^{7,15}.

Consider the reaction sequence:



where B^+ can be formed from many different precursors (A_i^+) in addition to A^+ . Also, A^+ can be a precursor forming different product ions (B_i^+) in addition to B^+ . If the magnetic field is set to monitor B^+ (B^+ is in resonance with the M.O.) without scanning the magnetic field, another radio frequency signal can be introduced into the ICR cell so that A^+ can gain power and be ejected. When this occurs, the

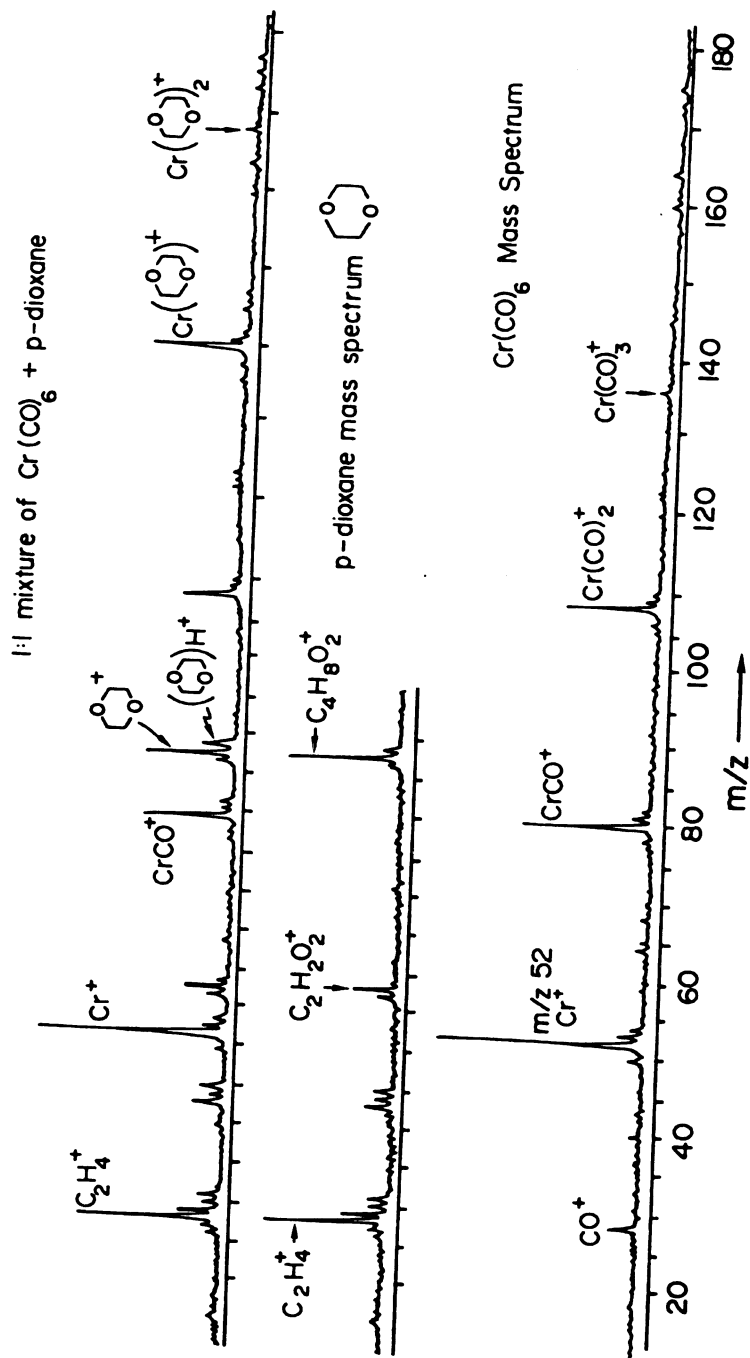


Figure 4. ICR Mass Spectra Of $\text{Cr}(\text{CO})_6^+$ P-dioxane
With Pressure Ratio 1 : 1 At Total
Pressure 1.0×10^{-5} torr

intensity of B^+ decreases. By scanning the frequency we applied to the cell, we can eject all possible precursors A_i^+ forming B^+ to get this "double resonance" response.

Remember

$$\omega_c = \frac{eB}{mc}$$

at constant B , $\omega_c M = \text{constant}$, therefore

$$\frac{\omega_{c1}}{\omega_{c2}} = \frac{m_2}{m_1}$$

It is then predictable at which frequency ratio the intensity of B^+ will decrease to indicate a unique reactant: product pair, since

$$\frac{\omega_A}{\omega_B} = \frac{m_B}{m_A} \quad \text{and} \quad \omega_B = 153 \text{ KHz}$$

Figure 5 shows a typical double resonance spectrum.

In earlier ICDR experiments⁸, the second oscillator was introduced in the analyzer region (on plates #5,6). This can lead to serious interference problems between this oscillator and the marginal oscillator which is also coupled to these plates. If applied in the source region, stronger second oscillating fields can be applied without affecting the marginal oscillator. Appendix D describes other alternatives.

3. ICR Facilities at Michigan State University

The ICR used in the experiments which will be discussed was built at MSU.

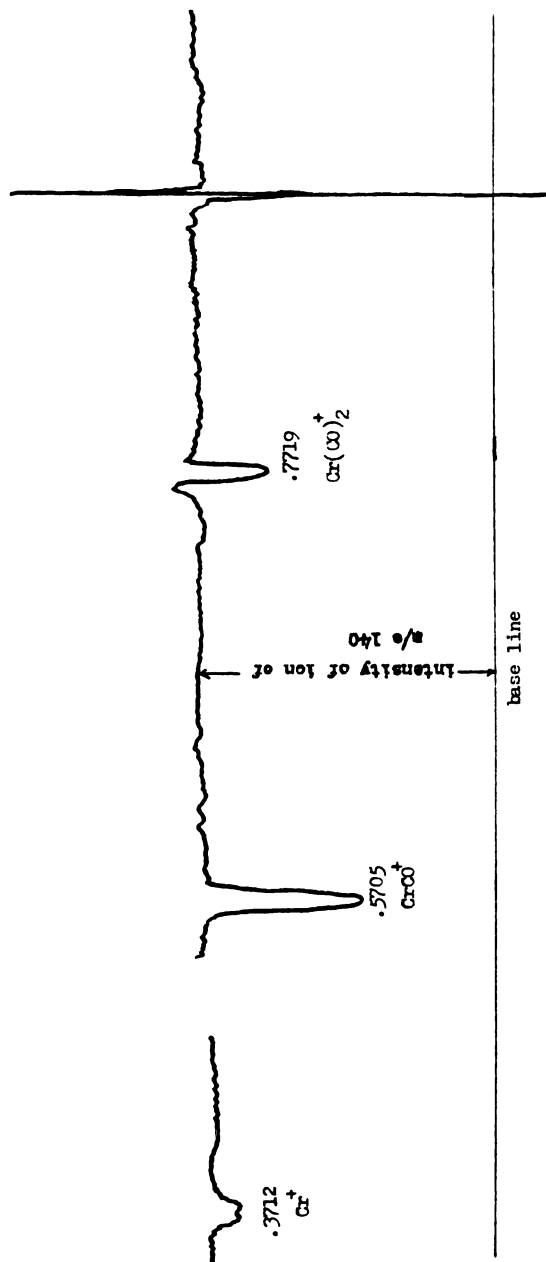


Figure 5. Double Resonance Spectrum Of $m/e \text{ } 140$
In Figure 4.

The filament emission controller and plate voltage controller for the ICR cell were designed and constructed by Dr. M. Raab and Dr. J. Allison in the Department of Chemistry at MSU. The marginal Oscillator detector is based on the design of Warnick, Anders and Sharp¹¹. A Wavetek model 144 sweep generator is used as the secondary oscillator in ICDR experiments. The ICR cell is housed in a stainless steel vacuum system and is situated between the pole-caps of a Varian 12" electromagnet (1.5" gap). The electromagnet is controlled by a Varian V-7800, 13 KW power supply and Fiedial Mark I magnetic field regulator.

The instrument is pumped by a 4" diffusion pump with a liquid nitrogen cold trap, and an Ultek 20 l/s ion pump controlled by an Ultek 150 mA ion pump controller made by Perkin-Elmer. The lock-in amplifier used to enhance S/N is model 128 A, (0.5 Hz - 1000 KHz) from EG&G Princeton Applied Research.

Samples are admitted from a dual inlet (separately pumped by a 2" diffusion pump and liquid nitrogen cold trap) by Varian 951-5106 precision leak valves. Approximate pressures are measured using a Veeco RG 1000 ionization guage.

4. Interpretation of Experimental Data

Data were acquired in the following manner. High and low pressure (1×10^{-5} torr vs. 1×10^{-6} torr) spectra of each compound were taken, and ion-molecule reaction products

in either "metal carbonyl" or "organic molecule only" experiments were determined. The "extra" peaks observed in the mixture were taken as ion-molecule reaction products formed in 1:1 or 1:2 mixtures (in pressure) of metal carbonyl to organic, at a total pressure of 1×10^{-5} torr as shown in Figure 4. All the product ions were then studied to unambiguously identify the precursor ions by the ICDR technique. The following points should be considered in the interpretation of ICR experiments.

a. Ions are produced with thermal velocities, since the ions are trapped by small trapping voltages. Fast ions will not be trapped and thus do not react with neutral molecules in these experiments.

The application of drift voltages only increases ion velocities by 10%. This contrasts with conventional mass spectrometers in which ion extraction from ion sources requires strong electric fields, accelerating ions to some keV energies.

b. Ions have relatively long residence times in the analyzer region. Residence times of milliseconds or more enable the observation of gas phase ion-molecule reactions. This contrasts with microsecond intervals in conventional mass spectrometers.

c. Low pressure experiments yield mass spectra with fragments experiencing no collisions. Table 1 shows the relationship between collisional parameters and pressure.

Appendix E shows how to calculate the Langevin collision rate, collision frequency and time between collisions.

d. At higher pressure, gas phase ion-molecule reactions are observed. From these, (1) kinetic studies can be performed; (2) double resonance can be used to identify reaction sequences; (3) branching ratios can be calculated. (Appendix F)

e. Various thermochemical quantities can be deduced from observed ion-molecule reactions. Upper and lower limits on heats of formation of charged and neutral species, and limits on bond strengths can be deduced. It is assumed that processes which are observed must be exothermic or thermoneutral.

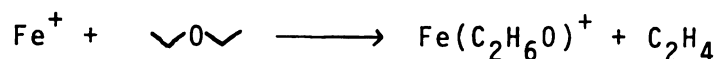
Table 1. Collisional Parameters As Functions
of Pressure For Co^+ Reaction With Et_2O

<u>Pressure</u> torr	<u>Time Between Collisions</u>		<u>Ion-Molecule^b</u> sec.
	<u>Number Density</u> molecules/cm ³	<u>Neutral-Neutral^a</u> sec.	
10 ⁻²	3.24 x 10 ¹⁴	1.68 x 10 ⁻⁵	2.67 x 10 ⁻⁶
10 ⁻³	3.24 x 10 ¹³	1.68 x 10 ⁻⁴	2.67 x 10 ⁻⁵
10 ⁻⁴	3.24 x 10 ¹²	1.68 x 10 ⁻³	2.67 x 10 ⁻⁴
10 ⁻⁵	3.24 x 10 ¹¹	1.68 x 10 ⁻²	2.67 x 10 ⁻³
10 ⁻⁶	3.24 x 10 ¹⁰	1.68 x 10 ⁻¹	2.67 x 10 ⁻²
10 ⁻⁷	3.24 x 10 ⁹	1.68	2.67 x 10 ⁻¹

a. Time between collisions¹: $Z_A^{-1} = \sqrt{mkt} / 4\sqrt{\pi} \sigma^2 p$

b. $\alpha(\text{Et}_2\text{O}) = 8.78 \times 10^{-24} \text{ cm}^3$, $K_L = 1.154 \times 10^{-9} \text{ cm}^3/\text{molecules}$, see Appendix E.

For example,



since $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \longrightarrow \text{C}_2\text{H}_5\text{OH} + \text{C}_2\text{H}_4 \quad \Delta H = 16.8 \text{ kcal/mole}^{18}$

therefore $D[\text{Fe}^+ - (\text{O} - \text{C}_2\text{H}_5)] > 16.8 \text{ kcal/mole},$

for the overall reaction to be exothermic.

f. Since most ion-molecule reactions occur with a rate that is within an order of magnitude of their pre exponential factor, $\sim 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, it is assumed that they occur with essentially no activation energy. This follows from the Arrhenius equation

$$k(T) = A e(-E_a/RT)$$

where A is on the order of $10^{10} \text{ l mol}^{-1} \text{ sec}^{-1}$, namely $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for bimolecular gas phase reactions.

g. In the absence of solvent, all of the energy of observed reactions must be accounted for by the products. Since we are assuming gas phase reactions are exothermic, the product ions formed must be more stable with respect to the reactants. In contrast, the energy can be dissipated through solvent molecules surrounding the product ions in solution. Because of this, there is rarely a single product in an ion molecule reaction ($\text{P}^+ + \text{N} \longrightarrow \text{I}^{+\star}$). Bonds are usually broken and $\text{I}^{+\star}$ fragments. At higher pressures, $\text{I}^{+\star}$ can be stabilized by collisions, which is then called an

"addition product" ($P^+ + 2N \longrightarrow I^{+*} + N \longrightarrow I^+ + N^*$).

h. For some endothermic reactions, the energy barrier can be overcome by raising the kinetic energy of a reactant¹⁹.

THE CHEMISTRY

B. THE CHEMISTRY

1. Purpose of Research In Gas Phase Organometallic Chemistry.

The work which will be described in this text deals with the gas phase chemistry of a number of metal- and metal-containing ions with various neutral organic substrates. The purposes of studying gas phase organometallic chemistry include the following:

- a. Gas phase results are used in kinetic theories²⁰⁻²¹.
- b. Gas phase reactions can be used to model condensed phase chemistry.

Catalysis draws tremendously broad interests and constitutes an important research field for chemists. Although there are a plethora of papers being published to probe the catalytic behavior observed in surface chemistry and homogeneous organometallic complexes²³, it is not well understood what occurs at a metal center due to the complication of ligand electronic effects³¹ for the former and solvent effects for the latter²⁴. On the other hand, researchers in heterogeneous metal catalysis²⁵ studies claimed that metal clusters play an important role in catalysts^{26,27}, which agrees with ab initio studies^{28,29} and can be used as an interface between molecular and solid state chemistry²⁷. Moreover metal-carbon double and triple bonds are frequently proposed in mechanisms for such reactions³⁰. However, all these fields have suffered from a lack of sufficient

thermochemical and structural information and are still inevitably somewhat speculative in nature. Building blocks of this nature allows the facile correlation of vast amounts of chemical data. Gas phase metal-ion/molecule reactions can serve this purpose. Other processes in organometallic chemistry whose gas phase ionic chemistry parallels can be readily studied are:

- 1) Hot atom chemistry³²
- 2) Atmospheric chemistry³³
- 3) Matrix isolation studies^{32,34}
- 4) Metal catalysis chemistry
- 5) Organometallic chemistry and the solution chemistry of metal complexes (e.g. ligand substitution reactions)

c. The study of reactivity trends

Gas phase ion-molecule reactions allow the investigator to study chemical dynamics and chemical events in the absence of solvent complications. At operating pressure ($10^{-5} \sim 10^{-6}$ torr) used in mass spectrometric techniques such as ICR and ion beam³⁵ experiments, single collision events (the basic unit of chemical reactions) can be studied, namely two species come together to react and separate as products. In this work, reactants are metal ions (M^+), metal-containing ions (ML_n^+) and organic neutrals (A). By varying M, L, and the structure of A, we can study how metal ions react, and what factors affect their reactivity, and thereby

characterize the mechanisms of such reactions.

d. Gas phase chemistry is suggestive of condensed phase processes

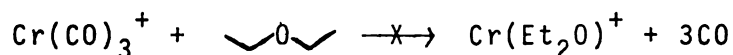
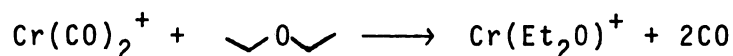
The results from gas phase chemical studies are often suggestive of condensed phase experiments. Recently, Kametani and Fukumoto³⁶ have demonstrated an intriguing technique called "retro mass spectral synthesis". Fragmentation of a compound on electron impact in a mass spectrometer is frequently very similar to chemical degradation reactions³⁹. For example, cyclohexene decomposes to give butadiene and ethylene. This compound fragments on electron impact to give $C_4H_6^+$ and C_2H_4 . Cyclohexene can also be synthesized by butadiene and ethylene by a Diels-Alder reaction. Mass spectral fragmentations frequently, therefore, parallel synthetic pathways as well as degradation pathways. Kametani and Fukumoto have used this observation to develop new synthetic pathways for a number of natural products³⁶.

There are many ion-molecule reactions in the gas phase having condensed phase analogs^{37,38}. Similarly, the nature of the bonding of organic molecules on metals can be understood from this work, which can be used to examine what has been proposed, for example, in methathesis³⁰.

e. Thermodynamics

Although reaction rates can theoretically provide an understanding of the effects of structure on reactivity in organometallic reactions, most observed reactions can be

understood in terms of thermodynamics. In other words, bond-strengths can be reflected in the reactivity as a driving force to initiate the reaction. Limits on heats of formation of various complexes, and limits on bondstrengths can also be obtained. Limits on $D(\text{ML}_n^+-\text{A})$ where A is an alkyl group, hydrogen atom, halogen atom, oxygen atom, alkoxy group, or various π and n-donor bases can also be obtained. For example, consider the reactions:

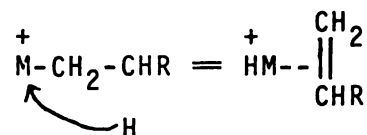


we found that $D(\text{Cr}^+-2\text{CO's}) = 66.2$ kcal/mole and $D(\text{Cr}^+-3\text{CO's}) = 87.7$ kcal/mole, therefore, we conclude that 66.2 kcal/mole $< D(\text{Cr}^+-\text{Et}_2\text{O}) < 87.7$ kcal/mole.

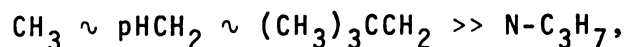
f. The study of mechanisms of organometallic reactions

Since organic molecules contain alkyl groups, the interaction of a metal center and an alkyl group is very important. The following mechanisms are found useful to explain reactions observed in the gas phase:

1. β -Elimination. This process involves the shift of a β -H atom from the alkyl group onto the metal⁴⁰⁻⁴².

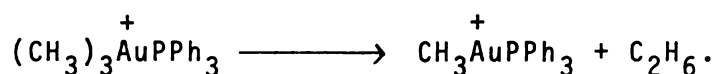
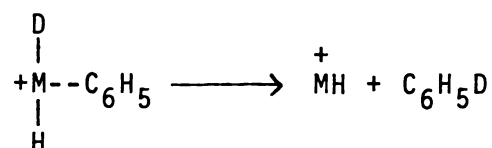


The relative stabilities of dialkyl compounds⁴³,



$\text{N-C}_4\text{H}_9 > \text{C}_2\text{H}_5 > \text{t-C}_4\text{H}_9 > \text{i-C}_3\text{H}_7$, shows the parallel to carbonium ion stabilities.

2. Reductive Elimination. This is a pathway for metal-carbon cleavage with β -atom migration^{40,44} e.g.



Other mechanisms proposed in catalytic studies^{40,45} have not been used in gas phase organometallic reactions yet.

The organometallic literature since 1960 has shown that the thermodynamics of bonding in organometallic compounds is of interest, however relatively few actual bond strengths have been measured. This can be done in gas phase reactions as described in b.

Table 2 summarizes the metal-ligand dissociation energies obtained from ion beam studies by J.L. Beauchamp, which will be of great use in interpretation of results in this thesis.

g. Li^+ use has been demonstrated as a mass chemical reagent¹⁹⁷. It gives simple spectra, easy to interpret.

Table 2. Summary of Metal-Ligand Bond
Dissociation Energies^a. (kcal/mol)

<u>R</u>	<u>Cr⁺-R</u>	<u>Mn⁺-R</u>	<u>Fe⁺-R</u>	<u>Co⁺-R</u>	<u>Ni⁺-R</u>
H	35 _± 4	53 _± 3	58 _± 5	52 _± 4	43 _± 2
CH ₃	37 _± 7	> 48	68 _± 4	61 _± 4	48 _± 5
CH ₂	65 _± 7	94 _± 7	96 _± 5	85 _± 7	86 _± 6
O	77 _± 5	57 _± 3	68 _± 3	65 _± 3	45 _± 4

a. Data were taken from ion beam studies by J.L. Beauchamp⁹⁴⁻⁹⁷.

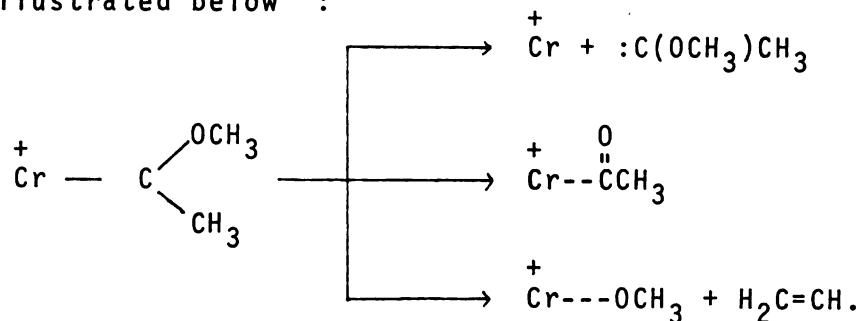
2. Historical Review of Transition Metal Ion Chemistry

From its birth through the mid 1960s, most of the applications of mass spectrometry have involved organic compounds. In the past two decades, however, applications have been extended into inorganic chemistry. Mass spectrometry is now commonly used to provide molecular weights and formulae of inorganic and organometallic compounds. Many thermodynamic data were obtained from this field. There are quite a few specific areas of interest in the general area of gas phase metal ion reactions:

a. Fragmentation Studies. (Unimolecular reactions)

Early work was devoted to investigations of the ionization potentials of organometallic compounds⁵², their fragmentation patterns, and how these are affected by ligands⁵³. Other

extensive studies of fragmentation patterns in main group organometallics^{50,54}, metal carbonyls⁵⁵, polynuclear metal carbonyls⁵⁰ and coordination compounds^{56,57} have been reported. A typical fragmentation following electron impact is illustrated below⁵⁸:



Most of this early work was done on volatile organometallic compounds, but, field desorption⁵⁹, and recently²⁵² Cf plasma desorption⁶⁰, laser desorption⁶¹, secondary ion⁶² and fast atom bombardment⁶³ techniques have made possible mass spectrometric studies on nonvolatile compounds and even ionic substances such as salts⁵⁹.

In addition, chemical ionization mass spectrometry (CIMS) studies have also been performed with organometallic compounds. Examples are CIMS (using CH₄) of sandwich compounds^{64,65}, metal hexacarbonyls⁶⁵, cyclopentadienyl metal halides⁶⁵, and arene metal carbonyls⁶⁴.

b. Photochemical Studies. The photodecomposition pathways of several metal carbonyl anions⁶⁶ such Ni(CO)₃⁻ and Co(CO)₄⁻ and cations⁶⁷ have yielded useful thermochemical data on metal carbonyl fragments, such as heats of formation and average bond energies as shown in Table III.

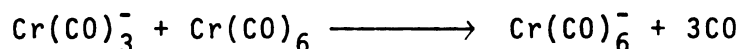
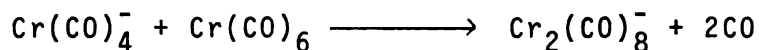
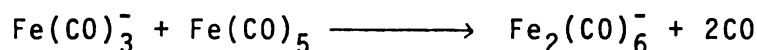
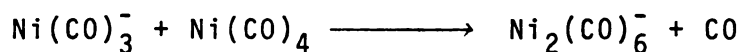
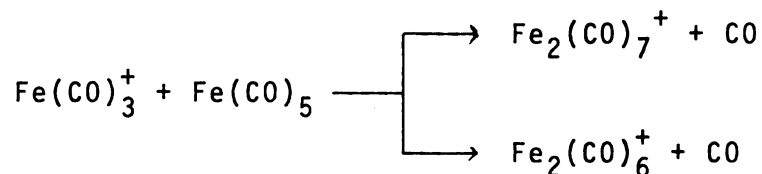
Table 3 . Heats Of Formation And Average Bond Energies Of The
Positive Ions From Fe(CO)₅ And Ni(CO)₄

	photoionization threshold(ev)	ΔH_f^0 ^a (ev)	Average bond energies
Fe(CO) ₅			D[Fe-(CO) ₅]=1.25±0.03ev
Fe(CO) ₅ ⁺	7.98±0.01	0.37±0.02	D[Fe-(CO) ₅]=1.23±0.03ev
Fe(CO) ₄ ⁺	8.77±0.1	2.31±0.1	
Fe(CO) ₃ ⁺	9.87±0.1	4.55±0.1	
Fe(CO) ₂ ⁺	10.68±0.1	6.51±0.1	
Fe CO ⁺	11.53±0.1	8.51±0.1	
Fe ⁺	14.03±0.1	12.35±0.1	
Ni(CO) ₄			D[Ni-(CO) ₄]=1.53±0.03ev
Ni(CO) ₄ ⁺	8.32±0.01	2.07±0.02	D[Ni-(CO) ₄]=1.36±0.03ev
Ni(CO) ₃ ⁺	8.77±0.02	3.58±0.02	
Ni(CO) ₂ ⁺	10.10±0.1	6.14±0.1	
NiCO ⁺	11.65±0.1	8.84±0.1	
Ni ⁺	13.75±0.1	12.09±0.1	

a. The assumed processes are $M(CO)_x + h\nu \longrightarrow [M(CO)_{x-n}]^+ + n CO$

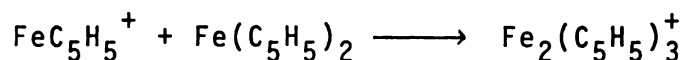
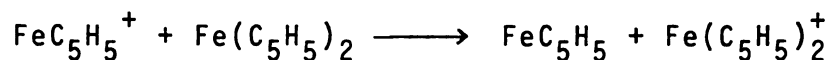
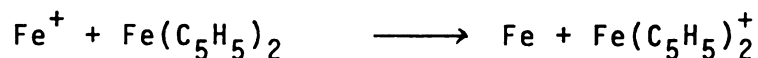
c. Gas Phase Ion-Molecule Reaction Chemistry in Organometallic Systems.

(i) Metal and Metal Containing Ion-Molecule Reaction with Organometallic Compounds. The formation of ions of the type $M_2(CO)_x^+$ from ion-molecule reactions in metal carbonyls have been reported for the group VI hexa-carbonyls^{55,68}. $Fe(CO)_5$ ⁶⁷⁻⁷¹ and the negative ion chemistry of Ni, Fe and Cr carbonyls⁷² (with accompanying loss of 1 or 2 CO groups) as follows:



Further reactions to produce tri-iron carbonyl ions ($Fe_3(CO)_y^+$), and the formation of ions up to $Fe_4(CO)_{12}^+$ were also observed. From these studies and ligand substitution studies⁷⁰ with a series of n- and π -donor bases, proton affinities (PA)^{70,72} of metal carbonyls and bond energies⁷⁰ can also be obtained. For example, P.A. ($Fe(CO)_5$) = 204 ± 3 kcal/mole; $D [H-Fe(CO)_5^+] = 23 \pm 10$ kcal/mole.

Also, the gas phase ion chemistry of ferrocene⁷³ and nickelocene⁷⁴ have been reported. Predominant features are charge transfer processes and the formation of a bimetallic complex $M_2(C_5H_5)_3^+$, e.g.



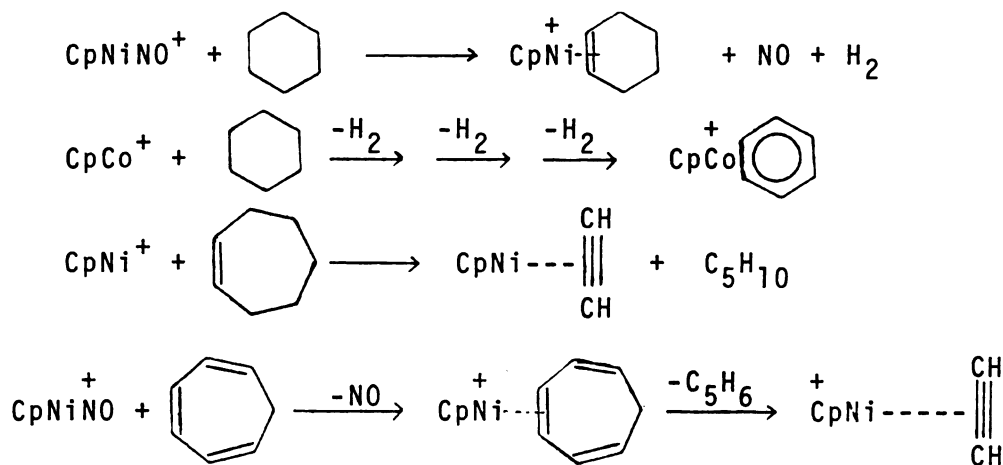
Also, "triple decker sandwich" complexes were reported for these compounds^{75,76}. From these studies, the proton affinity of $Ni(C_5H_5)_2$ was reported to be 218.9 ± 1.0 kcal/mole⁷⁴.

Müller also reported the gas phase ion chemistry of other sandwich compounds such as dibenzene chromium^{68,77}. He has also studied the chemistry of π - and n -donor bases with ions formed from electron impact on $C_5H_5CrC_6H_6$, $C_5H_5MnC_6H_6$, $C_5H_5VC_7H_7$, and $C_5H_5CrC_7H_7$ ⁷⁸.

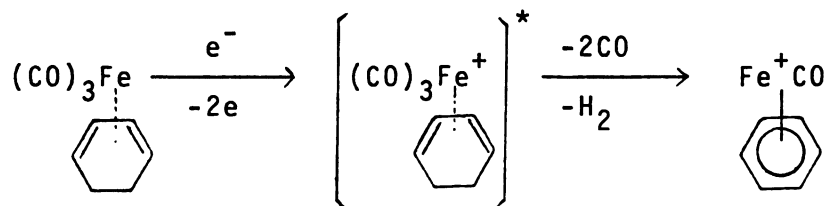
In addition, the ion-molecule reactions in $C_5H_5V(CO)_4$ ⁷, $C_5H_5Mn(CO)_3$ ⁷⁹ and $C_5H_5Cr(CO)_2NO$ ⁸⁸ have also been studied by Müller. The ionic chemistry in mixtures of $C_5H_5Mn(CO)_3$ with PF_3 , AsF_3 , SbF_3 and SF_4 was reported by Müller and Fendler⁷⁹. The ion-molecule chemistry of $CpNiNO$ ($Cp = C_5H_5$) and the chemistry of its ions with n - and π -donor bases were also reported^{80,81}. From this study, a series of $CpNi-B$ relative bond strengths were determined⁸¹.

(ii) Metal and Metal Containing Ion-Molecule

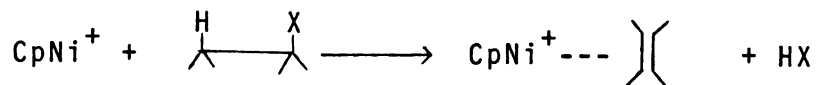
Reactions with Organic Neutral Compounds. J. Müller has studied the chemistry of metal-containing ions with hydrocarbons^{77,80}, in which H_2 loss with simultaneous formation of a new complex is observed:



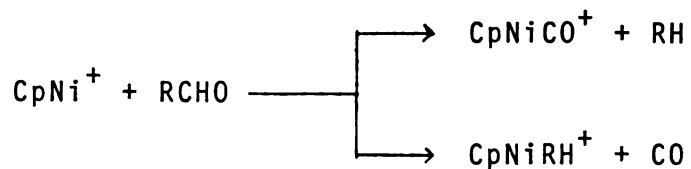
H_2 loss processes parallel the normal electron impact fragmentation mode for similar organometallic compounds⁵⁸, e.g.



J.L. Beauchamp has studied the gas phase chemistry of CpNi^+ with alkyl halides and found that the reduction⁸² of alkyl halides (RX) by CpNi^+ to olefins and HX is similar to that observed for Li^+ ⁸³.

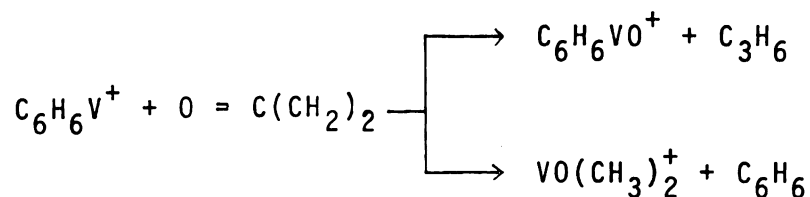


Decarbonylation of aldehydes was also observed⁸²:



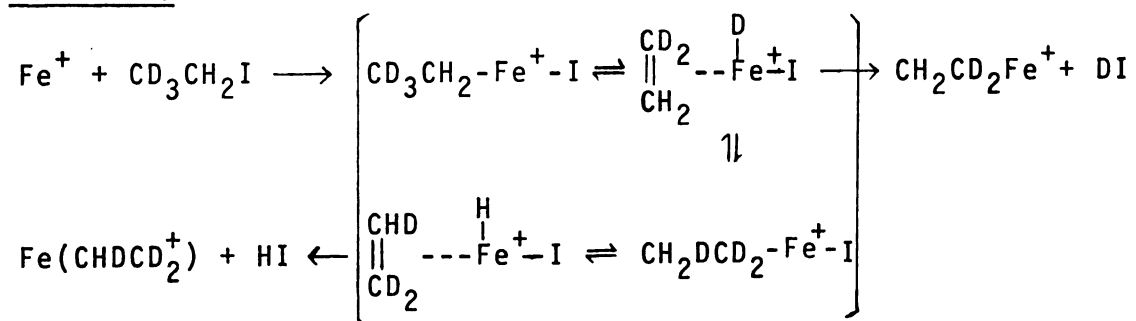
The energy profile for this process is shown in Fig. 6.

Deoxygenation of acetone by metal-containing ions have also been reported⁷⁸:



Recently, J. Allison and D.P. Ridge have studied the transition metal ions of iron, cobalt, and nickel with polar organic molecules and found that these transition metal ions always insert into a polar bond^{84,85} and is followed by a β -H atom shift (Scheme I):

Scheme I.



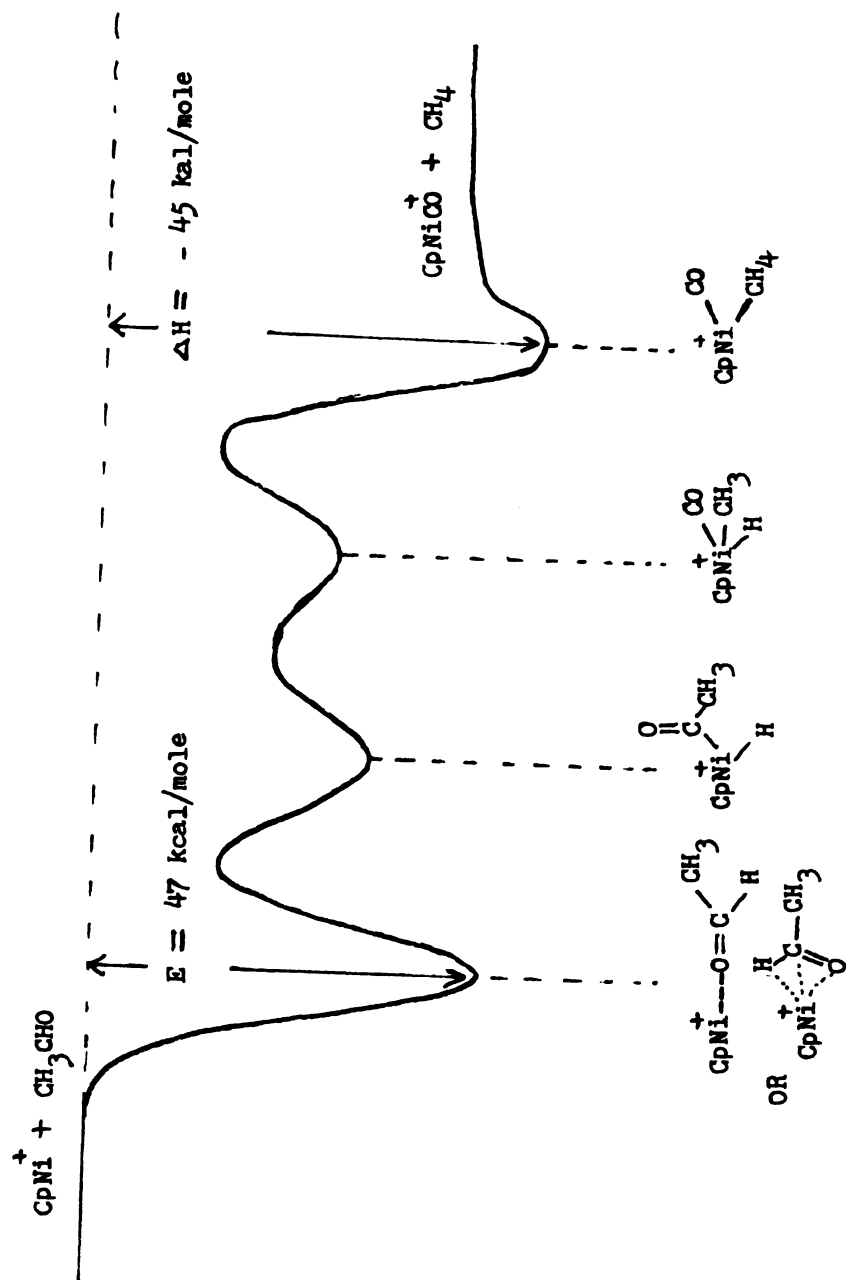


Figure 6. Energy Profile : CpNi^+ and CH_3CHO

This process is proposed to follow the reaction diagram of intermediates shown in Figure 7.

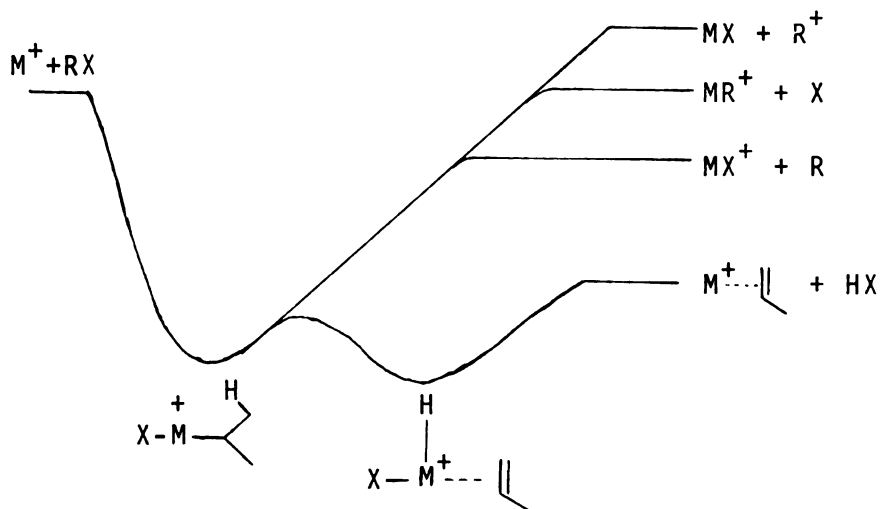
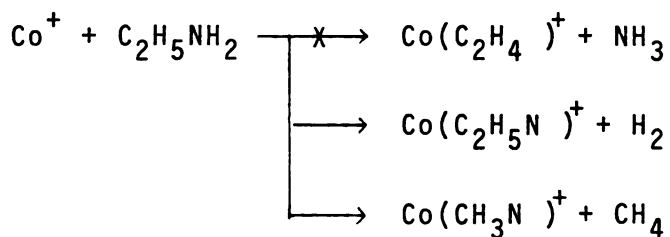
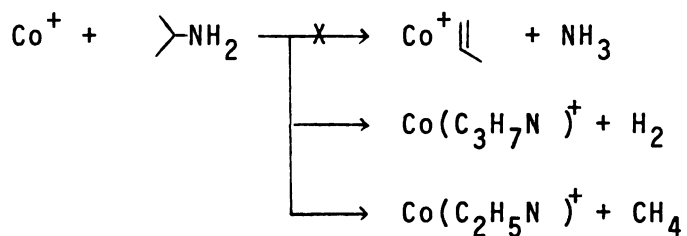
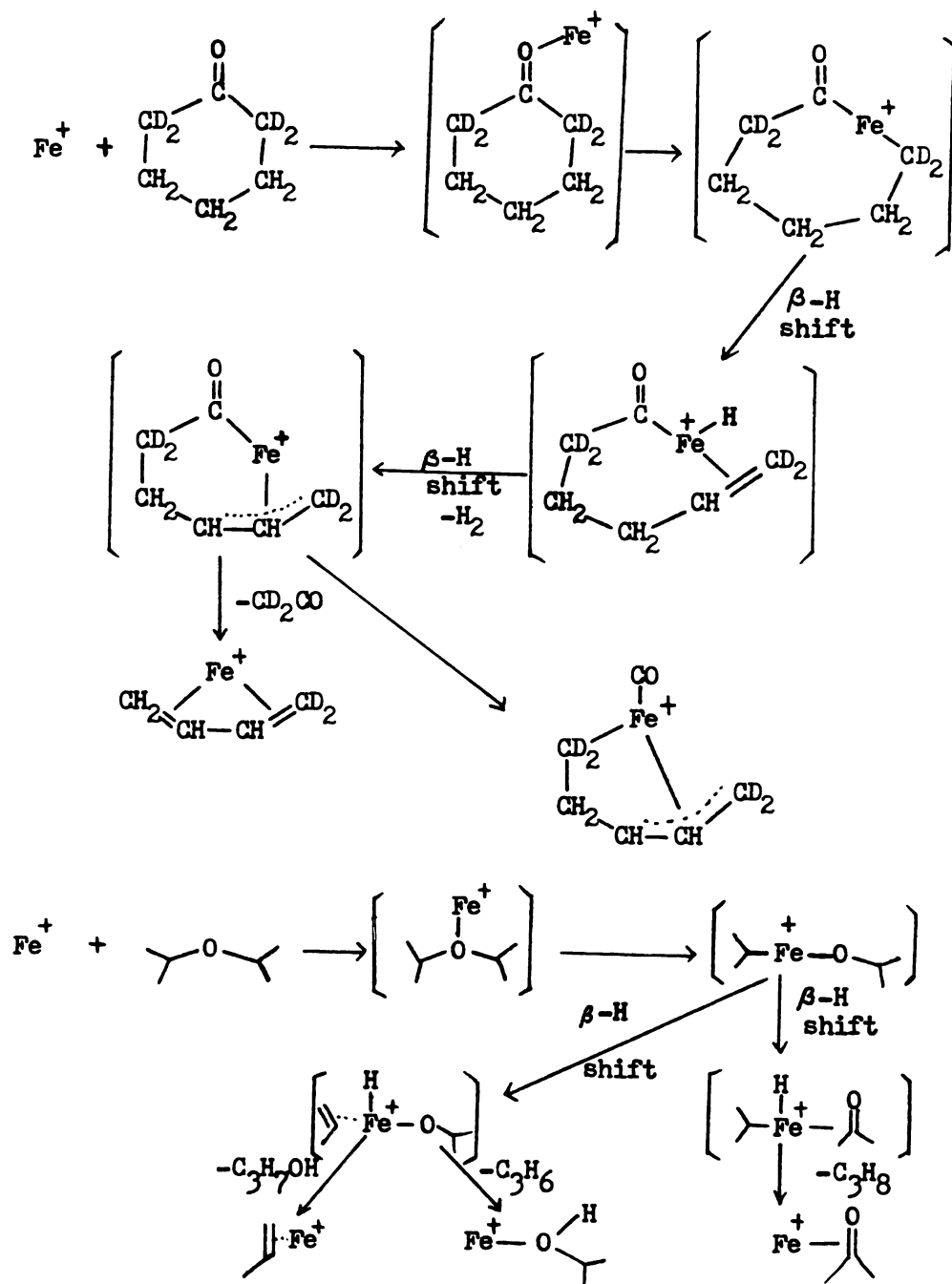


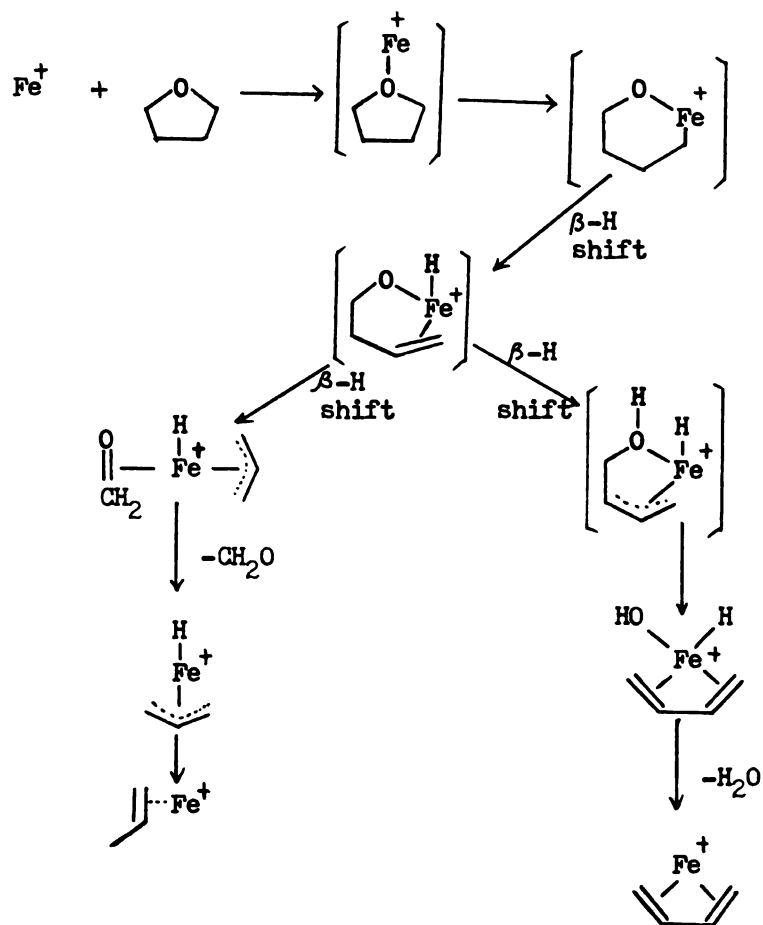
Figure 7. Schematic Representation of The Potential Energy Surface For The Reaction Of a Transition-Metal Ion With An Alkyl Halide.

However, this mechanism does not operate for amines⁸⁶:



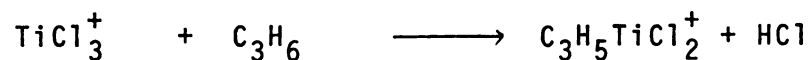
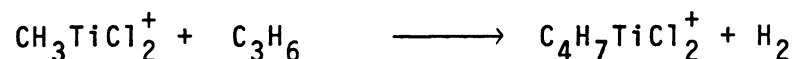
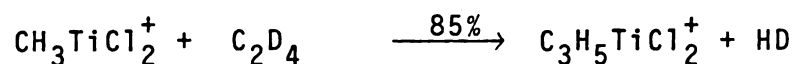
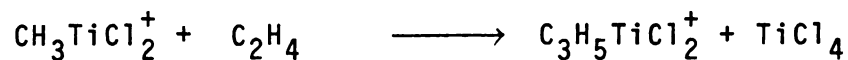
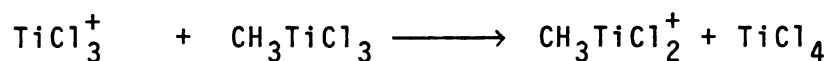
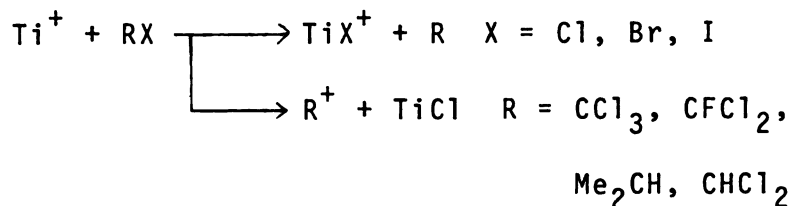
Scheme II (cont'd)



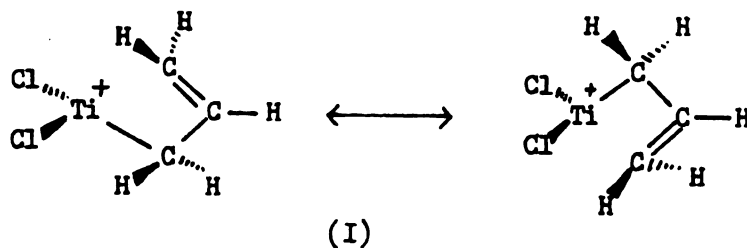
Scheme II (cont'd)

Hence, Fe^+ inserts into a carbonyl-carbon bond or a C-O bond in its reaction with ketones and ethers respectively and form a metalcyclic intermediate in its reaction with cyclic ketones and ethers. This is followed by a β -H shift, similar to that in Scheme I.

The study of the gas phase chemistry of titanium ions with haloalkanes⁸⁸, and alkenes⁸⁹ has also been reported, e.g.

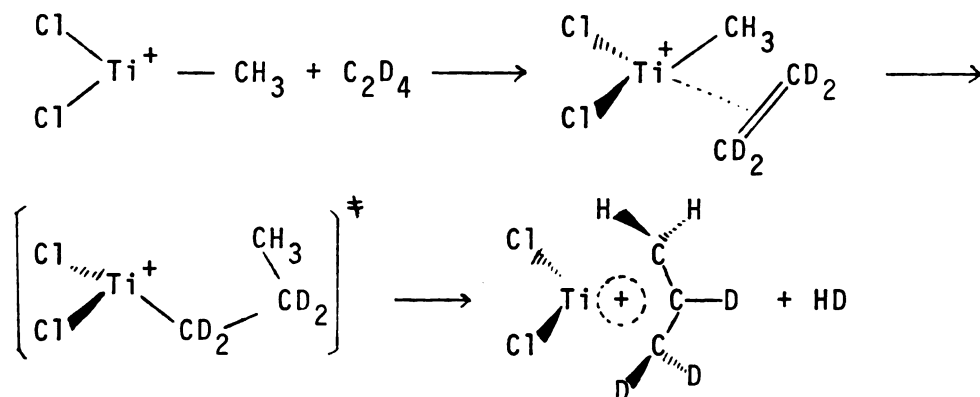


Note that titanium has only four valence sites. TiCl_3^+ reacts with C_3H_6 by eliminating HCl to give $\text{C}_3\text{H}_5\text{Ti}^+\text{Cl}_2$, probably being a resonance stabilized allyl- TiCl_2 cation (I) as shown below:



$\text{CH}_3\text{Ti}^+\text{Cl}_2$ reacts with C_2D_4 , 85% of the reaction proceeds by HD elimination. This suggests a mechanism (Scheme III), in which, after association with the Ti cation center, the C_2D_4 inserts into Ti—C bond of $\text{CH}_3\text{TiCl}_2^+$ as would occur in the polymerization of ethylene.

Scheme III.



The resulting species undergoes unimolecular decomposition because it is unable to dispose of its excess internal energy in this gas phase bimolecular process. Consequently, 1,2-elimination of HD across the β - and γ -carbons gives the allyl- TiCl_2^+ cation (I) and does not react further. To be effective, mediation of reactivity of $\text{CH}_3\text{TiCl}_2^+$ by solvent, the nearby presence of a counterion and another molecule such as AlMe_3 as in Ziegler-Natta catalysts are apparently necessary.

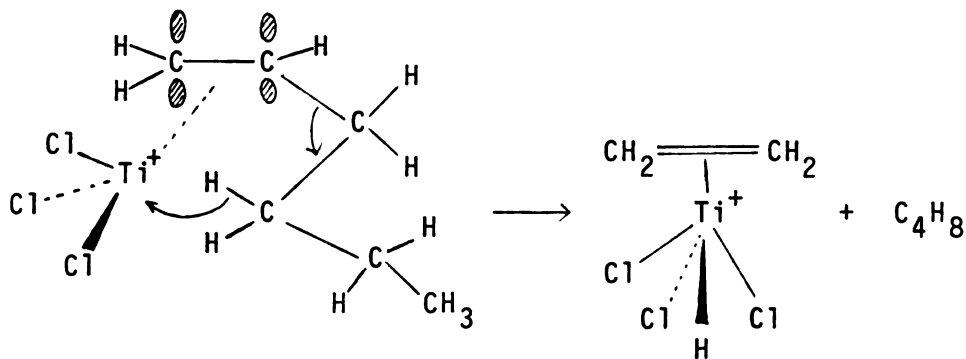
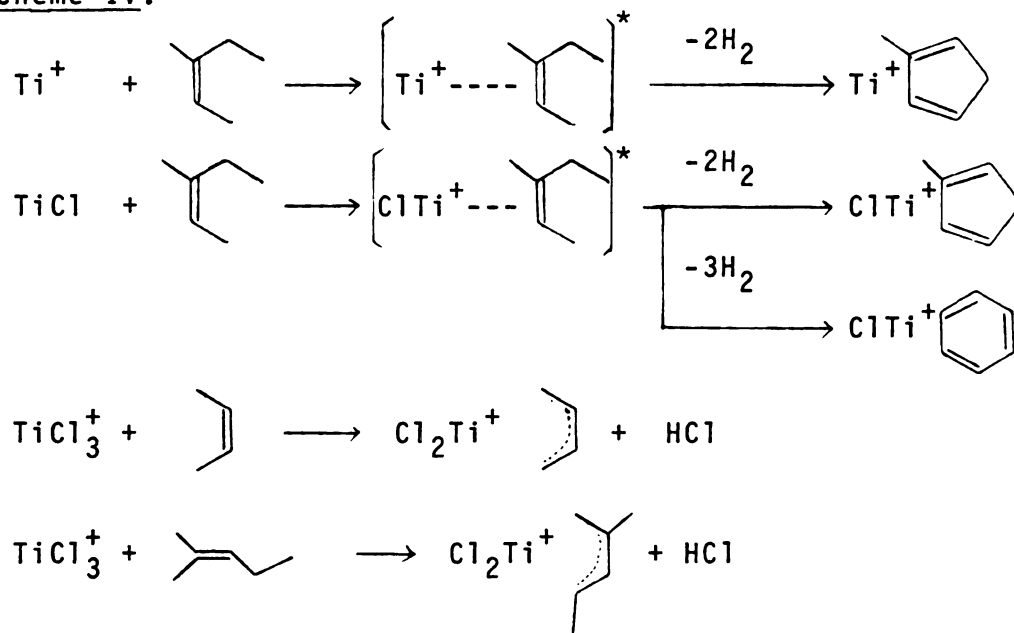
J. Allison and D.P. Ridge have also reported the chemistry of titanium containing ions with alkenes⁹⁰ and oxygen-containing organic compounds⁹¹ and reported the following

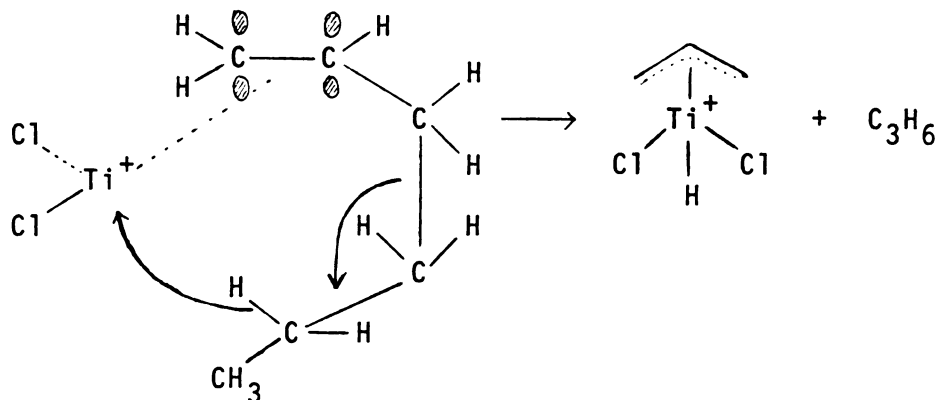
trends:

1. Ti^+ , TiCl^+ eliminate $n\text{H}_2$ with olefins ($n \geq 1$).
2. TiCl_2^+ , TiCl_3^+ eliminate HCl with olefins containing a carbon chain of ≤ 5 carbon atoms.
3. TiCl_2^+ , TiCl_3^+ eliminate small olefins from olefins containing a carbon chain of ≥ 6 carbon atoms.

Scheme IV shows these processes.

Scheme IV.

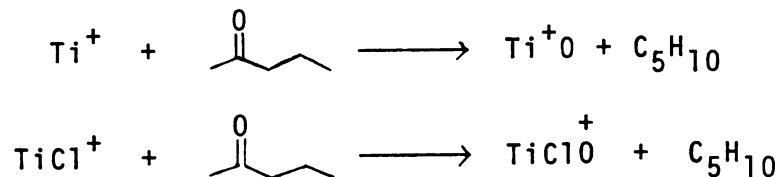


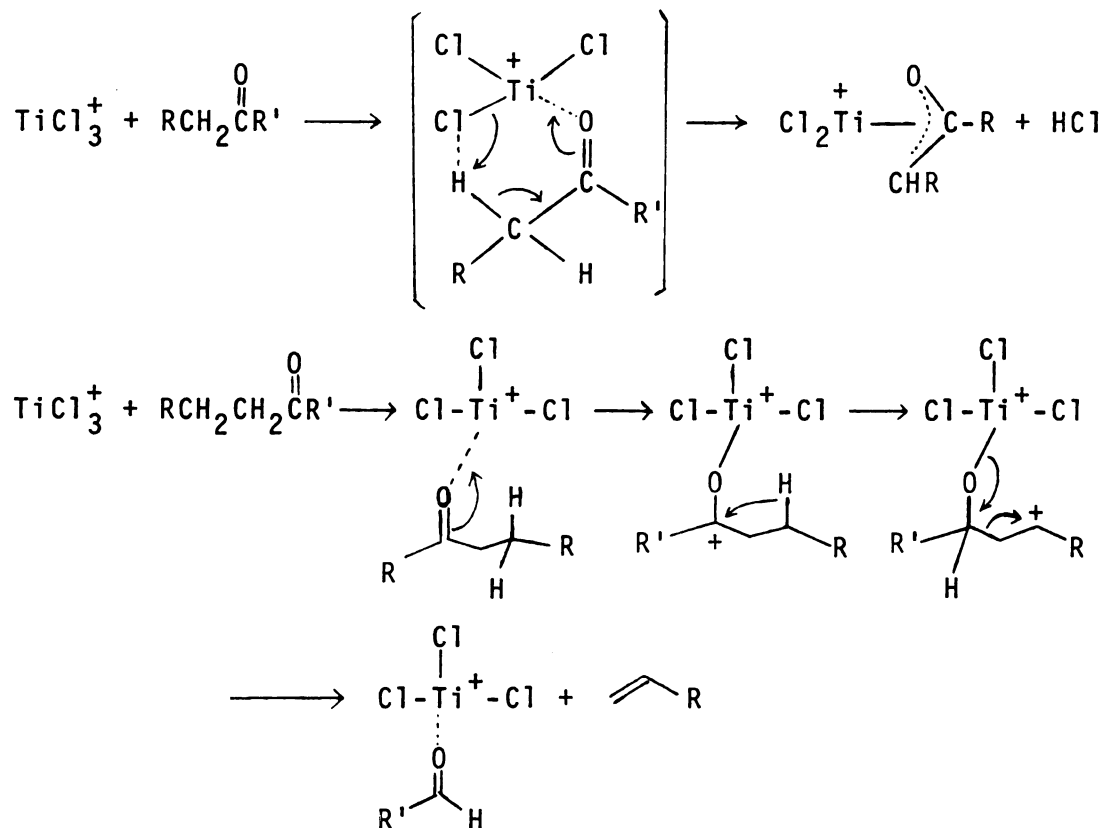
Scheme IV (cont'd)

For oxygen-containing organic compounds, the following trends were reported:

1. Ti^+ , TiCl^+ deoxygenate aldehydes and ketones.
2. TiCl_2^+ , TiCl_3^+ eliminate HCl with small aldehydes and ketones.
3. TiCl_2^+ , TiCl_3^+ eliminate small olefins from aldehydes and ketones containing ≥ 4 -carbon chains.

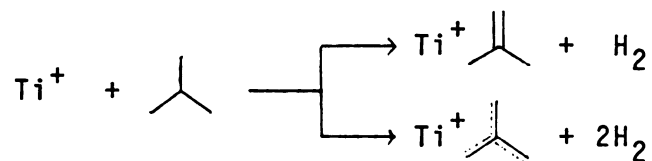
Scheme V shows reactions representative of these processes:

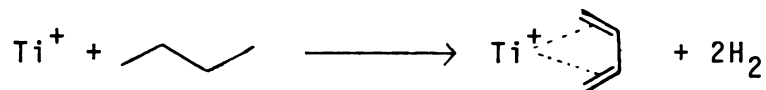
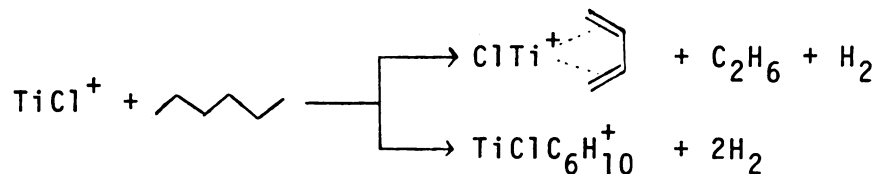
Scheme V.

Scheme V (cont'd)

Note that HCl and olefin eliminations proceed through a 6-membered ring intermediate with an α -hydrogen needed for the former process and a β -hydrogen for the latter.

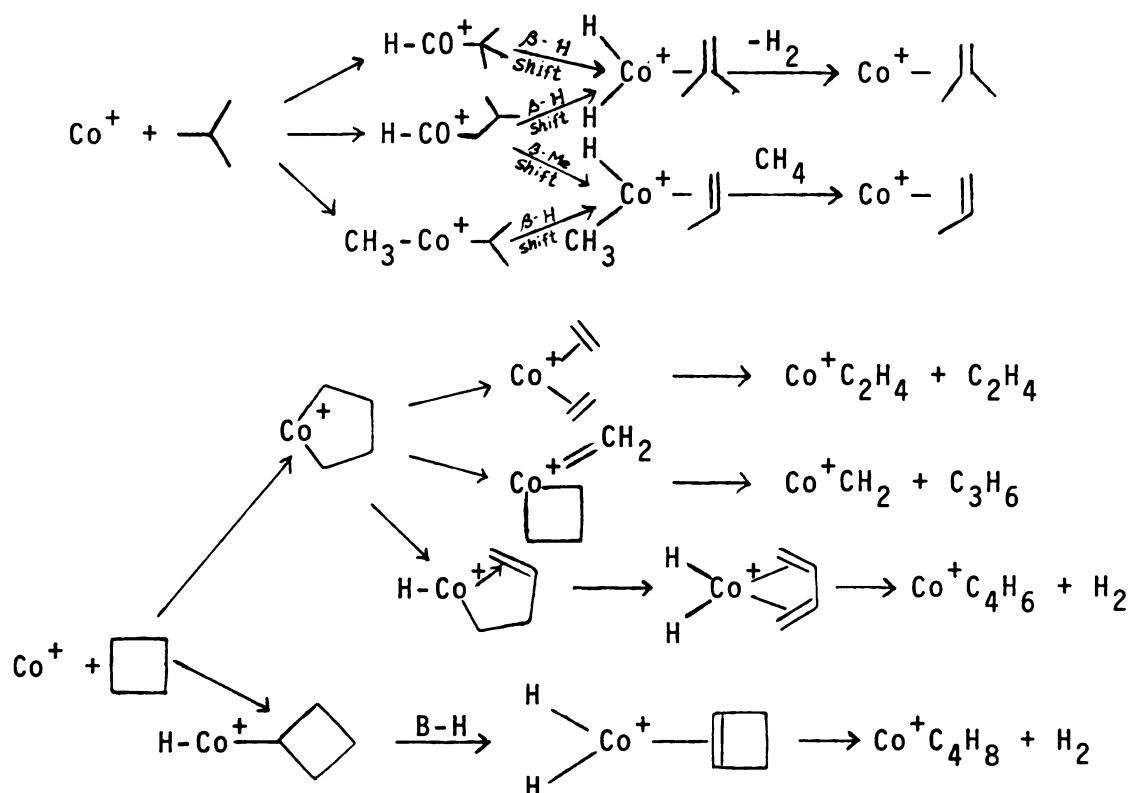
Ti^+ reactions with alkanes have also been studied^{92,93}, e.g.

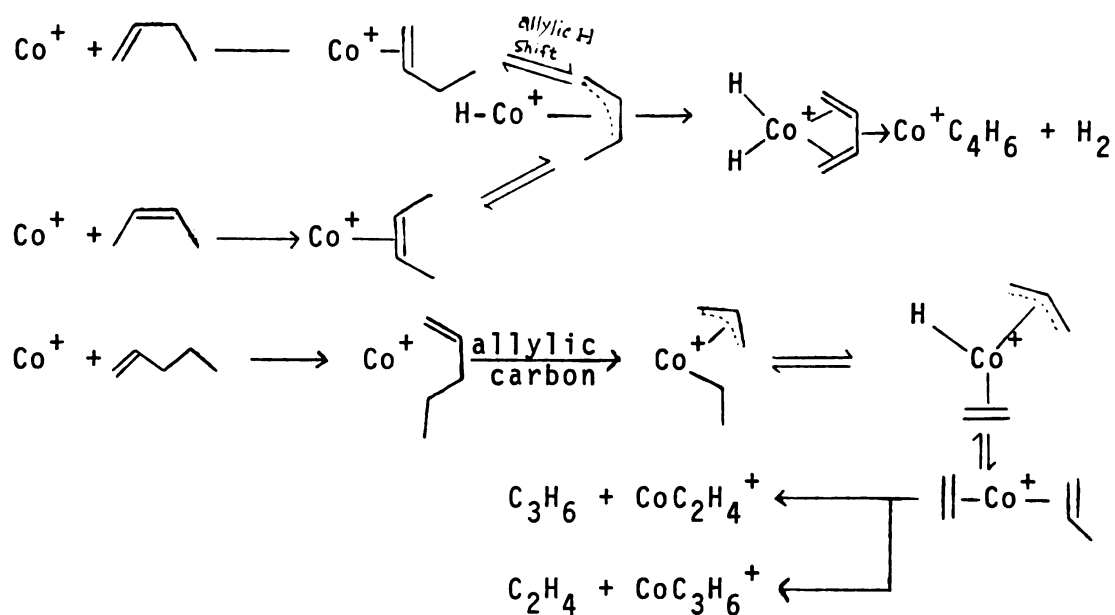




In contrast, transition metal ion chemistries with alkanes⁹⁴⁻⁹⁶ and alkenes⁹⁷ by ion beam studies were reported by J.L. Beauchamp as shown in Scheme VI and VII.

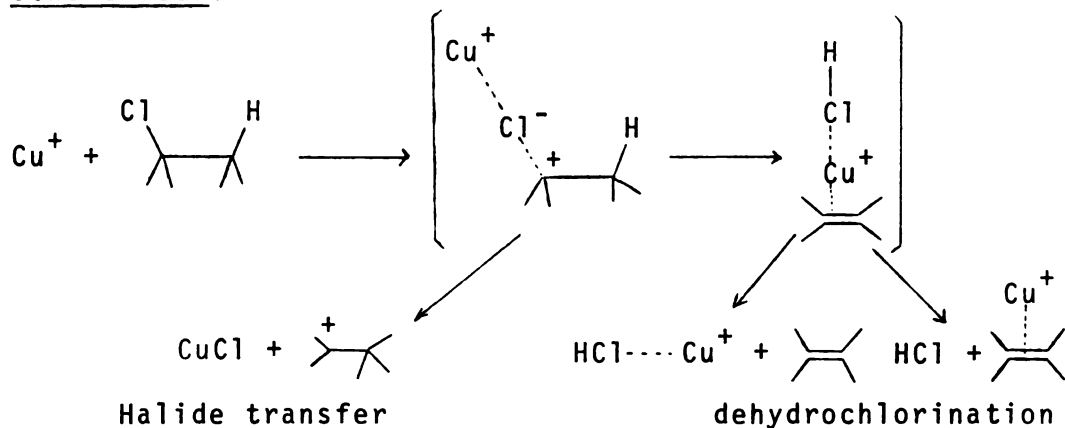
Scheme VI.



Scheme VII.

Hence, Co^+ can insert into either a C-H bond or a C-C bond followed by a β -H, β -methyl, allylic H, or allylic alkyl shift. Note that 1-butene can be isomerized to cis-2-butene and vice versa.

Copper, on the other hand, does not insert into carbon-polar bonds in alkyl halides⁹⁸, ketones and esters⁹⁹ (similar to Li^+ and Na^{+85}) as is shown in Schemes VIII and IX.

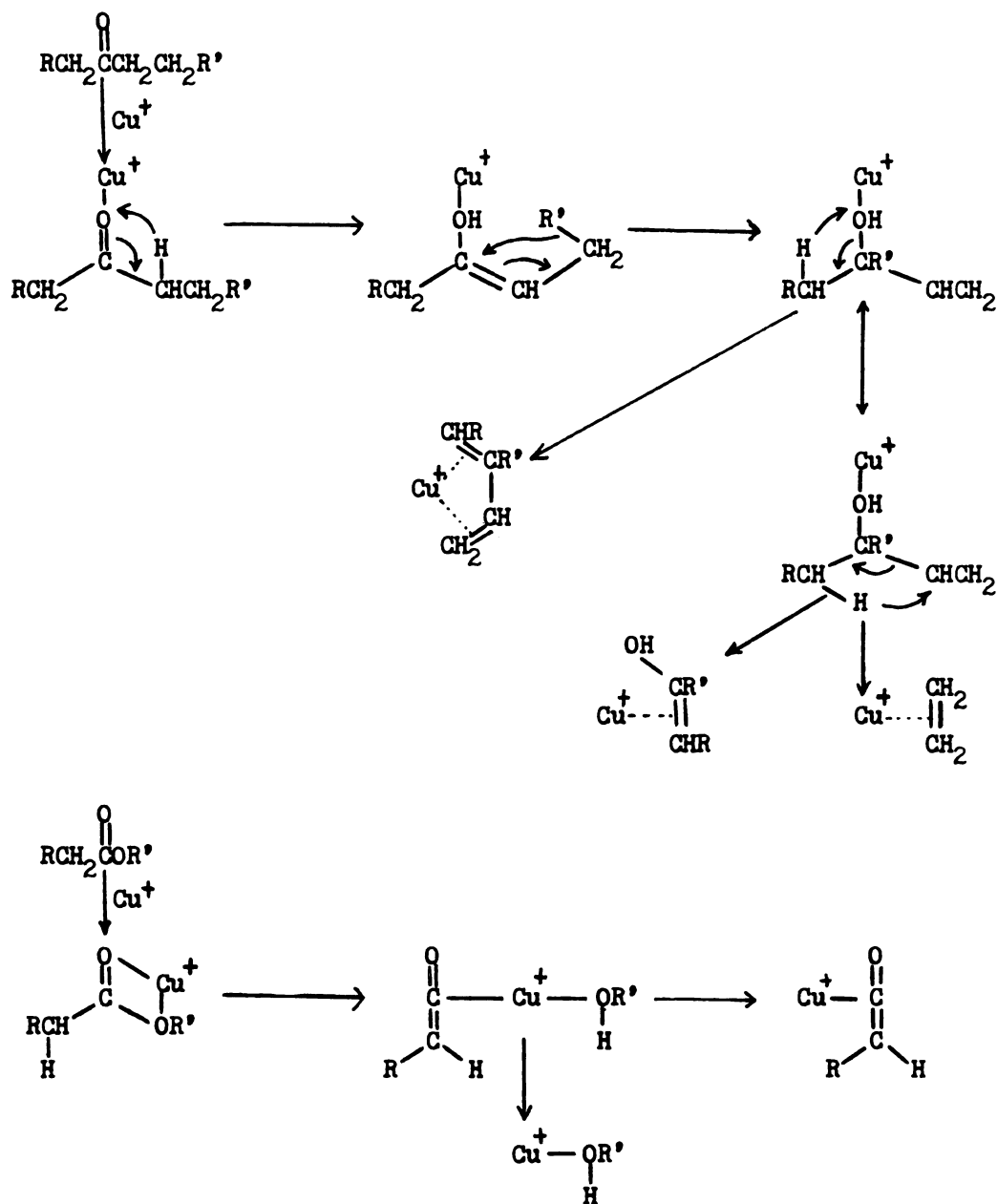
Scheme VIII.

In order to determine if the two groups in an organic molecule behave as one "new group", a study of cobalt with bifunctional organic molecules is being performed in our laboratory¹⁰⁰. Some important results are summarized below:

1. In the case of adjacent functional groups, it cannot be assumed that products indicative of each group will be observed in reactions with gaseous metal ions.

2. 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.

3. In the case of allyl amine, we do see strong evidence for insertion of Co^+ into the C-N bond in contrast with regular amines⁸⁶, presumably driven by the strong interaction with allyl group.

Scheme IX.

5. The adjacent groups in bifunctional ketones never react as one "new" functional group.

Hence, if two functional groups are in close proximity, the possibilities exist in which an attacking metal ion could (1) produce products indicative of both groups, (2) preferentially react with one group over another, or (3) react with both groups together as a new group.

The gas phase chemistry of metal and metal-containing ions with multifunctional organic molecules is the main work which will be discussed in this dissertation.

In conclusion, transition metal ions coordinate to the n-donor (O, X, N) or π -donor (double bonds) groups of organic molecules first. Then, they can either attract function groups (e.g. CpNi⁺) or polar atoms (e.g., V⁺, Cu⁺, Ti⁺) from the organic molecules directly or insert into carbon-polar bonds (e.g., Fe⁺, Co⁺, Ni⁺) or carbon-carbonyl bond (e.g., Fe⁺, Co⁺, Ni⁺) followed by β -hydrogen shifts to get corresponding products. Ti⁺ and Cu⁺ are unique. They prefer to retain oxygen and they do not insert into bonds, presumably due to weak bonding to carbon. Instead, they interact with heteroatoms strongly to direct energy for inducing rearrangements, namely, it also acts as a mediator.

Obviously, the reactions depend on both the metal and the organic molecule's structures and most of the experimental results can be explained in terms of bond strengths and thermodynamics which are involved.

Large molecules with multifunctional groups are complicated. In order to understand the gas phase chemistry of metal and metal containing ions with multifunctional organic compounds, we have to understand the configurational, and conformational effects of multi-functional organic compounds.

3. Multifunctional Molecules: The Macrocyclic Effect

The chelate effect has long been known in coordination chemistry to lead to increased stability of complexes. A macrocyclic effect in which the stability of a copper complex is additionally enhanced (10,000 more stable) by coordination to a tetraamine macrocyclic ligand compared to similar noncyclic tetraamine ligands has been reported¹¹³. The macrocyclic effect of crown ethers such as 18-crown-6 has also been reported to decrease when the dielectric constant of the medium increases¹⁰⁶. In the gas phase, in the absence of complicating solvent phenomena, an intrinsic macrocyclic effect is observed, which will be discussed in this text.

4. The Gas Phase Chemistry of Iron, Nickel and Chromium Ions and Their CO Containing Ions with Linear Ethers, Cyclic Ethers, Cyclic Polyethers and Crown Ethers.

Na^+ , K^+ , Mg^+ , and Ca^+ play vital roles in biological systems^{114,115, 116}, many of which are not understood as yet. Because in vivo complexation and decomplexation of the concerned cations take place essentially with macromolecular

bimolecules, and in vitro systems the macromolecular ligands¹¹⁷ have proved to be more efficient ligands than the conventional ones, the use of macromolecular ligands, especially crown ethers has become important.

Since the interaction of transition metal ions with crown ethers has not been previously reported, the decision was made to probe their intrinsic interactions in the gas phase in the absence of complicating solvent phenomena.

Iron, chromium and nickel ions were chosen for these studies because they exhibit quite different chemistries with organic molecules (see section 5).

In this work, $\text{Fe}(\text{CO})_5$, triethylene glycol diemthyl ether(TDE), 12-crown-4 and p-dioxane- d_8 were obtained from Aldrich Chemical Company. $\text{Co}(\text{CO})_3\text{NO}$, $\text{Cr}(\text{CO})_6$ and $\text{Ni}(\text{CO})_4$ were obtained from Alfa products. Tetrahydropyran (THP), 1,3-dioxolan and 1,3-dioxane were obtained from Fluka Chemical Company. Diethylether, p-dioxane and tetrahydrofuran (THF) were obtained from Mallinckrodt, Inc. Dimethylether was obtained from Matheson Medical Products Inc. and 15-crown-5 was obtained from PCR Research Chemicals, Inc. Dithylether, THF, 12-crown-4 and 15-crown-5 were refluxed with excess Na metal for 12 hours, then vacuum distilled under N_2 to remove H_2O . All compounds were subject to standard freeze-pump-thaw cycles before use.

I. $\text{Fe}(\text{CO})_x^+$ Reactions With Ethers And Polyethers.

A. Results

1. Linear Ethers and Polyethers

a. $\text{Fe}(\text{CO})_x^+$ reactions with dimethylether
($\text{C}_2\text{H}_6\text{O}$).

Ions formed as products of ion-molecule reactions in a mixture of $\text{Fe}(\text{CO})_5$ and dimethylether are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
86	$\text{Fe}(\text{CH}_2\text{O})^+$	Fe^+
102	$\text{Fe}(\text{C}_2\text{H}_6\text{O})^+$	Fe^+ , FeCO^+
130	$\text{FeCO}(\text{C}_2\text{H}_6\text{O})^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$
132	$\text{Fe}(\text{CH}_2\text{O})(\text{C}_2\text{H}_6\text{O})^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{C}_2\text{H}_6\text{O})^+$
133	$\text{Fe}(\text{CH}_3\text{O})(\text{C}_2\text{H}_6\text{O})^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{C}_2\text{H}_6\text{O})^+$
148	$\text{Fe}(\text{C}_2\text{H}_6\text{O})_2^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$
158	$\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_6\text{O})^+$	$\text{Fe}(\text{CO})_3^+$, $\text{Fe}(\text{CO})_4^+$
176	$\text{FeCO}(\text{C}_2\text{H}_6\text{O})_2^+$	$\text{Fe}(\text{CO})_4^+$
186	$\text{Fe}(\text{CO})_3(\text{C}_2\text{H}_6\text{O})^+$	$\text{Fe}(\text{CO})_4^+$
214	$\text{Fe}_2(\text{CO})_2(\text{C}_2\text{H}_6\text{O})^+$	Fe^+ , $\text{Fe}(\text{CO})_5^+$
242	$\text{Fe}_2(\text{CO})_3(\text{C}_2\text{H}_6\text{O})^+$	Fe^+ , FeCO^+ , $\text{Fe}_2(\text{CO})_4^+$

b. $\text{Fe}(\text{CO})_x^+$ reactions with diethylether
(C_4H_{10}).

Ions formed as products of ion-molecule reactions in a mixture of $\text{Fe}(\text{CO})_5$ and diethylether are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
84	$\text{Fe}(\text{C}_2\text{H}_4)^+$	Fe^+
100	$\text{Fe}(\text{C}_2\text{H}_4\text{O})^+$	Fe^+ , FeCO^+
102	$\text{Fe}(\text{C}_2\text{H}_5\text{OH})^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$
128	$\text{Fe}(\text{C}_4\text{H}_8\text{O})^+$	Fe^+ , FeCO^+
130	$\text{Fe}(\text{C}_4\text{H}_{10}\text{O})^+$	FeCO^+ , $\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$
158	$\text{FeCO}(\text{C}_4\text{H}_{10}\text{O})^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$, $\text{Fe}(\text{CO})_4^+$
175	$\text{Fe}(\text{OC}_2\text{H}_5)(\text{C}_4\text{H}_{10}\text{O})^+$	FeCO^+ , $\text{Fe}(\text{C}_4\text{H}_{10}\text{O})^+$
186	$\text{Fe}(\text{CO})_2(\text{C}_4\text{H}_{10}\text{O})^+$	$\text{Fe}(\text{CO})_4^+$
197	$\text{Fe}(\text{CO})_5\text{H}^+$	$\text{C}_2\text{H}_5\text{O}^+$
204	$\text{Fe}(\text{C}_4\text{H}_{10}\text{O})_2^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$, $\text{FeCO}(\text{C}_4\text{H}_{10}\text{O})^+$
214	$\text{Fe}(\text{CO})_3(\text{C}_4\text{H}_{10}\text{O})^+$	$\text{Fe}(\text{CO})_4^+$, $\text{Fe}(\text{CO})_5^+$
232	$\text{FeCO}(\text{C}_4\text{H}_{10}\text{O})_2^+$	$\text{Fe}(\text{CO})_4^+$, $\text{Fe}(\text{CO})_2(\text{C}_4\text{H}_{10}\text{O})^+$, $\text{Fe}(\text{CO})_5^+$, $\text{Fe}(\text{CO})_3(\text{C}_4\text{H}_{10}\text{O})^+$
242	$\text{Fe}(\text{CO})_4(\text{C}_4\text{H}_{10}\text{O})^+$	Fe^+ , $\text{Fe}(\text{CO})_5^+$

Note that $\text{Fe}(\text{C}_2\text{H}_4)^+$ has the same mass as FeCO^+ . However, FeCO^+ does not have any precursors, but $\text{Fe}(\text{C}_2\text{H}_4)^+$ has the precursor of Fe^+ . Therefore, m/e 84 is assigned as $\text{Fe}(\text{C}_2\text{H}_4)^+$ instead of FeCO^+ . Also, the ion at m/e 197 is formed by the proton transfer of $\text{C}_2\text{H}_5\text{O}^+$ to natural $\text{Fe}(\text{CO})_5$ as proved by double resonance experiments.

c. $\text{Fe}(\text{CO})_x^+$ reactions with triethylene glycol dimethylether ($\text{C}_8\text{H}_{18}\text{O}_4$, TDE)

Ions formed as products of ion-molecule reactions in a mixture of $\text{Fe}(\text{CO})_5$ and TDE are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
114	$\text{FeC}_3\text{H}_6\text{O}^+$	Fe^+ , FeCO^+
132	$\text{FeC}_3\text{H}_8\text{O}_2^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$
142	$\text{FeCOC}_3\text{H}_6\text{O}^+$	$\text{Fe}(\text{CO})_2^+$
144	$\text{FeCOC}_3\text{H}_8\text{O}^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$
158	$\text{FeCOC}_3\text{H}_6\text{O}_2^+$	$\text{Fe}(\text{CO})_4^+$
160	$\text{FeCOC}_3\text{H}_8\text{O}_2^+$	$\text{Fe}(\text{CO})_4^+$
170	$\text{Fe}(\text{CO})_2\text{C}_3\text{H}_6\text{O}^+$	$\text{Fe}(\text{CO})_2^+$
172	$\text{FeCOC}_4\text{H}_8\text{O}_2^+$	FeCO^+ , $\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$
188	$\text{Fe}(\text{CO})_2\text{C}_3\text{H}_8\text{O}_2^+$	$\text{Fe}(\text{CO})_3^+$, $\text{Fe}(\text{CO})_3^+$, $\text{Fe}(\text{CO})_4^+$
202	$\text{Fe}(\text{CO})_2\text{C}_4\text{H}_{10}\text{O}_2^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$, $\text{Fe}(\text{CO})_4^+$

2. Cyclic Ethers and Polyethers.

a. $\text{Fe}(\text{CO})_x^+$ reactions with tetrahydrofuran (THF, $\text{C}_4\text{H}_8\text{O}$)

Ions formed as products of ion-molecule reactions in a mixture of $\text{Fe}(\text{CO})_5$ and THF are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
98	$\text{Fe}(\text{C}_3\text{H}_6)^+$	Fe^+ , FeCO^+
110	$\text{Fe}(\text{C}_4\text{H}_6)^+$	Fe^+ , FeCO^+
128	$\text{Fe}(\text{C}_4\text{H}_8\text{O})^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{C}_3\text{H}_6)^+$
156	$\text{FeCO}(\text{C}_4\text{H}_8\text{O})^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$
158	$\text{Fe}(\text{CH}_2\text{O})(\text{C}_4\text{H}_8\text{O})^+$	FeCO^+ , $\text{Fe}(\text{CO})_2^+$
170	$\text{Fe}(\text{C}_3\text{H}_6)(\text{C}_4\text{H}_8\text{O})^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{C}_3\text{H}_6)^+$, $\text{Fe}(\text{C}_4\text{H}_8\text{O})^+$

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
170	$\text{Fe}(\text{C}_3\text{H}_6)(\text{C}_4\text{H}_8\text{O})^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$ $\text{Fe}(\text{C}_3\text{H}_6)^+$, $\text{Fe}(\text{C}_4\text{H}_8\text{O})^+$
184	$\text{Fe}(\text{CO})_2(\text{THF})^+$	$\text{Fe}(\text{CO})_4^+$
200	$\text{Fe}(\text{C}_4\text{H}_8\text{O})_2^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$, $\text{Fe}(\text{CO})_4^+$ $\text{FeCO}(\text{C}_4\text{H}_8\text{O})^+$
212	$\text{Fe}(\text{CO})_3(\text{C}_4\text{H}_8\text{O})^+$	$\text{Fe}(\text{CO})_4^+$, $\text{Fe}(\text{CO})_5^+$
228	$\text{FeCO}(\text{C}_4\text{H}_8\text{O})_2^+$	$\text{Fe}(\text{CO})_4^+$, $\text{Fe}(\text{CO})_5^+$ $\text{Fe}(\text{CO})_3^+(\text{C}_4\text{H}_8\text{O})$
240	$\text{Fe}(\text{CO})_4(\text{C}_4\text{H}_8\text{O})^+$	Fe^+ , $\text{Fe}(\text{CO})_5^+$
256	$\text{Fe}(\text{CO})_2(\text{C}_4\text{H}_8\text{O})_2^+$	$\text{Fe}(\text{CO})_5^+$, $\text{Fe}(\text{CO})_3(\text{C}_4\text{H}_8\text{O})^+$
268	$\text{Fe}_2(\text{CO})_3(\text{C}_4\text{H}_8\text{O})^+$	Fe^+ , FeCO^+ , $\text{Fe}_2(\text{CO})_4^+$, $\text{Fe}_2(\text{CO})_5^+$

b. $\text{Fe}(\text{CO})_x^+$ reactions with tetrahydropyran
(THP, $\text{C}_5\text{H}_{10}\text{O}$)

Ions formed as products of ion-molecule reactions in a mixture of $\text{Fe}(\text{CO})_5$ and THP are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
110	$\text{Fe}(\text{C}_4\text{H}_6)^+$	Fe^+
112	$\text{Fe}(\text{C}_4\text{H}_8)^+$	Fe^+
114	$\text{Fe}(\text{C}_3\text{H}_6\text{O})^+$	Fe^+
142	$\text{Fe}(\text{C}_5\text{H}_{10}\text{O})^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$
153	$\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_5)^+$	C_3H_5^+
170	$\text{FeCO}(\text{C}_5\text{H}_{10}\text{O})^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$
198	$\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_{10}\text{O})^+$	$\text{Fe}(\text{CO})_4^+$

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
211	$\text{FeCO}(\text{C}_5\text{H}_{10}\text{O})(\text{C}_3\text{H}_5)^+$	C_3H_5^+
226	$\text{Fe}(\text{CO})_3(\text{C}_5\text{H}_{10}\text{O})^+$	$\text{Fe}(\text{CO})_4^+$, $\text{Fe}(\text{CO})_5^+$
228	$\text{Fe}(\text{C}_5\text{H}_{10}\text{O})_2^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$, $\text{FeCO}(\text{C}_5\text{H}_{10}\text{O})^+$
254	$\text{Fe}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{O})^+$	Fe^+ , $\text{Fe}(\text{CO})_5^+$
256	$\text{FeCO}(\text{C}_5\text{H}_{10}\text{O})_2^+$	$\text{Fe}(\text{CO})_4^+$, $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_{10}\text{O})^+$

where ions at m/e 153 and 211 were formed from C_3H_5^+ reactions with $\text{Fe}(\text{CO})_5$. This has been observed previously⁸⁵.

c. $\text{Fe}(\text{CO})_x^+$ reactions with 1,3-dioxolan
 $(\text{C}_3\text{H}_6\text{O}_2)$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Fe}(\text{CO})_5$ and 1,3 dioxolan are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
84	$\text{Fe}(\text{C}_2\text{H}_4)^+$	Fe^+ , $\text{C}_3\text{H}_5\text{O}_2^+$
86	$\text{Fe}(\text{CH}_2\text{O})^+$	Fe^+
100	$\text{Fe}(\text{C}_2\text{H}_4\text{O})^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$, $\text{C}_3\text{H}_5\text{O}_2^+$
102	$\text{Fe}(\text{CH}_2\text{O}_2)^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$
114	$\text{Fe}(\text{C}_2\text{H}_2\text{O}_2)^+$	Fe^+ , FeCO^+
116	$\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{C}_2\text{H}_4\text{O})^+$
130	$\text{Fe}(\text{C}_3\text{H}_6\text{O}_2)^+$	FeCO^+ , $\text{Fe}(\text{CO})_2^+$
144	$\text{Fe}(\text{C}_2\text{H}_4\text{O})_2^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$ $\text{Fe}(\text{C}_2\text{H}_4\text{O})^+$, $\text{Fe}(\text{C}_3\text{H}_6\text{O}_2)^+$
154	$\text{Fe}(\text{CO})_2(\text{C}_2\text{H}_2\text{O})^+$	$\text{C}_2\text{H}_4\text{O}^+$

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
158	$\text{FeCO}(\text{C}_3\text{H}_6\text{O}_2)^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$
160	$\text{Fe}(\text{CH}_2\text{O})(\text{C}_3\text{H}_6\text{O}_2)^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{C}_3\text{H}_6\text{O}_2)^+$
174	$\text{Fe}(\text{C}_2\text{H}_4\text{O})(\text{C}_3\text{H}_6\text{O}_2)^+$	FeCO^+ , $\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{C}_3\text{H}_6\text{O}_2)^+$ $\text{FeCO}(\text{C}_3\text{H}_6\text{O}_2)^+$
186	$\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_6\text{O})^+$	$\text{Fe}(\text{CO})_3^+$, $\text{Fe}(\text{CO})_4^+$
204	$\text{Fe}(\text{C}_3\text{H}_6\text{O}_2)_2^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$, $\text{FeCO}(\text{C}_3\text{H}_6\text{O}_2)^+$
214	$\text{Fe}(\text{CO})_3(\text{C}_3\text{H}_6\text{O}_2)^+$	$\text{Fe}(\text{CO})_4^+$, $\text{Fe}(\text{CO})_5^+$
232	$\text{FeCO}(\text{C}_3\text{H}_6\text{O}_2)_2^+$	$\text{Fe}(\text{CO})_4^+$, $\text{Fe}(\text{CO})_2(\text{C}_3\text{H}_6\text{O})^+$

Note that the ions at m/e 84, 100 are assigned to be $\text{Fe}(\text{C}_2\text{H}_4)^+$ and $\text{Fe}(\text{C}_2\text{H}_4\text{O})^+$ respectively instead of FeCO^+ and $\text{Fe}(\text{CO}_2)^+$ as proved by double resonance experiments.

d. $\text{Fe}(\text{CO})_x^+$ reactions with 1,3 dioxane
 $(\text{C}_4\text{H}_8\text{O}_2)$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Fe}(\text{CO})_5$ and 1,3 dioxane are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
84	$\text{Fe}(\text{C}_2\text{H}_4)^+$	Fe^+
86	$\text{Fe}(\text{CH}_2\text{O})^+$	Fe^+
114	$\text{Fe}(\text{C}_2\text{H}_2\text{O}_2)^+$	Fe^+ , FeCO^+
115	$\text{FeCO}(\text{OCH}_3)^+$	$\text{C}_3\text{H}_5\text{O}^+$
116	$\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)^+$	Fe^+ , FeCO^+
142	$\text{FeCO}(\text{C}_3\text{H}_6\text{O})^+$ or $\text{FeCO}(\text{C}_2\text{H}_2\text{O}_2)^+$	FeCO^+

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
144	$\text{Fe}(\text{C}_4\text{H}_8\text{O}_2)^+$	FeCO^+ , $\text{Fe}(\text{CO})_2^+$
169	$\text{Fe}(\text{CO})_4\text{H}^+$	C_2H_5^+ , CH_3O^+
172	$\text{FeCO}(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$
174	$\text{Fe}(\text{CH}_2\text{O})(\text{C}_4\text{H}_8\text{O}_2)^+$	Fe^+ , FeCO^+
197	$\text{Fe}(\text{CO})_5\text{H}^+$	CH_3O^+ , $\text{C}_2\text{H}_3\text{O}_2^+$
200	$\text{Fe}(\text{CO})_2(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Fe}(\text{CO})_4^+$
228	$\text{Fe}(\text{CO})_3(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Fe}(\text{CO})_4^+$, $\text{Fe}(\text{CO})_5^+$
232	$\text{Fe}(\text{C}_4\text{H}_8\text{O}_2)_2^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$, $\text{FeCO}(\text{C}_4\text{H}_8\text{O}_2)^+$

The ion at m/e 115 is formed from the ion-molecule reactions of $\text{C}_3\text{H}_5\text{O}^+$ with neutral $\text{Fe}(\text{CO})_5$; m/e 169 is a proton transfer product from ethyl and methoxy ions.

e. $\text{Fe}(\text{CO})_x^+$ reactions with p-dioxane
 $(\text{C}_4\text{H}_8\text{O}_2)$ and d₈-p-dioxane

Since $\text{Fe}(\text{C}_2\text{H}_2\text{O}_2)^+$ has the same mass as $\text{Fe}(\text{C}_3\text{H}_6\text{O})^+$, $\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)^+$ has the same mass as $\text{Fe}(\text{C}_3\text{H}_8\text{O})^+$, and $\text{Fe}(\text{C}_2\text{H}_4)^+$ has the same mass as FeCO^+ , p-dioxane-d₈ was also studied in an attempt to resolve these assignments. Table 4 shows the ions formed as products of ion-molecule reactions in a mixture of each separately. All the precursors of products are identified by double resonance.

Note that in p-dioxane, the product at m/e 84 is $\text{Fe}(\text{C}_2\text{H}_4)^+$ and not FeCO^+ , since we observe m/e 88 in p-dioxane-d₈. Moreover, the FeCO^+ in " $\text{Fe}(\text{CO})_5$ only" does not have any reaction precursors, it is only found by electron impact on

Table 4 . $\text{Fe}(\text{O})_5$ Reactions With p-dioxane And p-dioxane d_8

p-dioxane			p-dioxane d_8		
m/e	stoichiometry	precursor(s)	m/e	stoichiometry	precursor(s)
84	$\text{Fe}(\text{C}_2\text{H}_4)^+$	Fe^+	88	$\text{Fe}(\text{CD}_2\text{O})^+ \text{Fe}(\text{C}_2\text{D}_4)^+$	Fe^+
86	$\text{Fe}(\text{CH}_2\text{O})^+$	Fe^+	120	$\text{Fe}(\text{C}_3\text{D}_6\text{O})^+$	$\text{Fe}^+, \text{FeCO}^+, \text{Fe}(\text{O})_2^+$
114	$\text{Fe}(\text{C}_3\text{H}_6\text{O})^+$	$\text{Fe}^+, \text{FeCO}^+$		$\text{Fe}(\text{C}_2\text{D}_4\text{O}_2)^+$	
116	$\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)^+$	$\text{Fe}^+, \text{FeCO}^+$	152	$\text{Fe}(\text{C}_4\text{D}_8\text{O}_2)^+$	$\text{FeCO}^+, \text{Fe}(\text{O})_2^+$
144	$\text{Fe}(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{FeCO}^+, \text{Fe}(\text{O})_2^+$	180	$\text{FeCO}(\text{C}_4\text{D}_8\text{O}_2)^+$	$\text{Fe}(\text{O})_2^+, \text{Fe}(\text{O})_3^+$
172	$\text{FeCO}(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Fe}(\text{O})_2^+, \text{Fe}(\text{O})_3^+$	184	$\text{Fe}(\text{CD}_2\text{O})(\text{C}_4\text{D}_8\text{O}_2)^+$	$\text{Fe}^+, \text{FeCO}^+, \text{Fe}(\text{O})_2^+$
174	$\text{Fe}(\text{CH}_2\text{O})(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{FeCO}^+, \text{Fe}(\text{O})_2^+$		$\text{Fe}(\text{C}_3\text{D}_6\text{O})^+$	$\text{Fe}(\text{C}_3\text{D}_6\text{O})^+$
		$\text{Fe}(\text{C}_4\text{H}_8\text{O}_2)^+$		$\text{Fe}(\text{C}_4\text{D}_8\text{O}_2)^+$	$\text{Fe}(\text{C}_4\text{D}_8\text{O}_2)^+$
200	$\text{Fe}(\text{O})_2(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Fe}(\text{O})_4^+$	208	$\text{Fe}(\text{O})_2(\text{C}_4\text{D}_8\text{O}_2)^+$	$\text{Fe}(\text{O})_4^+$
228	$\text{Fe}(\text{O})_3(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Fe}(\text{O})_4^+$	236	$\text{Fe}(\text{O})_3(\text{C}_4\text{D}_8\text{O}_2)^+$	$\text{Fe}(\text{O})_4^+, \text{Fe}(\text{O})_5^+$
232	$\text{Fe}(\text{C}_4\text{H}_8\text{O}_2)_2^+$	$\text{FeCO}^+, \text{Fe}(\text{O})_2^+, \text{Fe}(\text{O})_3^+$	248	$\text{Fe}(\text{C}_4\text{D}_8\text{O}_2)_2^+$	$\text{FeCO}^+, \text{Fe}(\text{O})_2^+, \text{Fe}(\text{O})_3^+$
256	$\text{Fe}(\text{O})_4(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Fe}^+, \text{Fe}(\text{O})_5^+, \text{Fe}_2(\text{O})_4^+$	264	$\text{Fe}(\text{O})_4(\text{C}_4\text{D}_8\text{O}_2)^+$	$\text{Fe}^+, \text{Fe}(\text{O})_5^+$
260	$\text{FeCO}(\text{C}_4\text{H}_8\text{O}_2)_2^+$	$\text{Fe}(\text{O})_4^+, \text{Fe}(\text{O})_2(\text{C}_4\text{H}_8\text{O}_2)^+$			

$\text{Fe}(\text{CO})_5$. Therefore, m/e 88 in p -dioxane- d_8 should be both $\text{Fe}(\text{C}_2\text{D}_4)^+$ and $\text{Fe}(\text{CD}_2\text{O})^+$. Likewise m/e 120 should be a mixture of $\text{Fe}(\text{C}_3\text{D}_6\text{O})^+$ and $\text{Fe}(\text{C}_2\text{D}_4\text{O}_2)^+$ corresponding to m/e 114 and 116 in the p -dioxane case. Also, m/e 184 could be a mixture of $\text{Fe}(\text{CD}_2\text{O})(\text{C}_4\text{D}_8\text{O}_2)^+$ and $\text{Fe}(\text{C}_3\text{D}_6\text{O})_2^+$, however, the latter species is absent in the p -dioxane study.

f. $\text{Fe}(\text{CO})_x^+$ reactions with 12-crown-4
 $(\text{C}_8\text{H}_{16}\text{O}_4)$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Fe}(\text{CO})_5$ and 12-crown-4 are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
98	$\text{FeC}_2\text{H}_2\text{O}^+$	Fe^+ , FeCO^+
114	$\text{FeC}_2\text{H}_2\text{O}_2^+$	Fe^+ , FeCO^+
116	$\text{FeC}_3\text{H}_8\text{O}^+$	Fe^+
124	$\text{FeC}_4\text{H}_4\text{O}^+$	Fe^+
126	$\text{FeC}_4\text{H}_6\text{O}^+$	Fe^+ , FeCO^+
130	$\text{FeC}_4\text{H}_{10}\text{O}^+$	Fe^+
	or $\text{FeC}_3\text{H}_6\text{O}_2^+$	
142	$\text{FeCOC}_2\text{H}_2\text{O}_2^+$	$\text{Fe}(\text{CO})_2^+$
144	$\text{FeC}_4\text{H}_8\text{O}_2^+$	Fe^+ , FeCO^+
160	$\text{FeC}_4\text{H}_8\text{O}_3^+$	Fe^+ , FeCO^+
174	$\text{FeC}_6\text{H}_{14}\text{O}_2^+$	Fe^+ , FeCO^+
204	$\text{FeC}_6\text{H}_{12}\text{O}_4^+$	FeCO^+ , $\text{Fe}(\text{CO})_2^+$

Note that m/e 130 could be either $\text{FeC}_4\text{H}_{10}\text{O}^+$ or

$\text{FeC}_3\text{H}_6\text{O}_2^+$ or a mixture of both. However, $\text{FeC}_4\text{H}_{10}\text{O}^+$ is easily explained by the mechanism which will be proposed in the discussion section.

g. $\text{Fe}(\text{CO})_x^+$ reactions with 15-crown-5 ($\text{C}_{10}\text{H}_{20}\text{O}_5$)

Ions formed as products of ion-molecule reactions in a mixture of $\text{Fe}(\text{CO})_5$ and 15-crown-5 are listed below, with their precursors as identified by double resonance techniques.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
100	$\text{Fe}(\text{C}_2\text{H}_4\text{O})^+$	FeCO^+
102	$\text{Fe}(\text{C}_2\text{H}_6\text{O})^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$
103	$\text{C}_4\text{H}_7\text{O}_3^+$ or $\text{C}_5\text{H}_{11}\text{O}_2^+$	$\text{C}_2\text{H}_3\text{O}_2^+$
114	$\text{Fe}(\text{C}_2\text{H}_2\text{O}_2)^+$	Fe^+ , FeCO^+
116	$\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)^+$	Fe^+ , FeCO^+
117	$\text{C}_6\text{H}_{13}\text{O}_2^+$	$\text{C}_4\text{H}_9\text{O}^+$ or $\text{C}_3\text{H}_5\text{O}_2^+$
118	$\text{Fe}(\text{C}_2\text{H}_6\text{O}_2)^+$	$\text{Fe}(\text{CO})_2^+$
144	$\text{Fe}(\text{C}_4\text{H}_8\text{O}_2)^+$	Fe^+ , FeCO^+
146	$\text{FeCO}(\text{C}_2\text{H}_6\text{O}_2)^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$, $\text{Fe}(\text{CO})_4^+$
160	$\text{Fe}(\text{C}_4\text{H}_8\text{O}_3)^+$	Fe^+
174	$\text{Fe}(\text{C}_6\text{H}_{14}\text{O}_2)^+$	Fe^+ , FeCO^+
177	$\text{C}_8\text{H}_{17}\text{O}_4^+$	$\text{C}_4\text{H}_9\text{O}_2^+$
204	$\text{Fe}(\text{C}_6\text{H}_{12}\text{O}_4)^+$	FeCO^+ , $\text{Fe}(\text{CO})_2^+$
211	$\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_3\text{O})^+$	$\text{C}_2\text{H}_3\text{O}^+$
214	$\text{Fe}(\text{C}_8\text{H}_{14}\text{O}_3)^+$	Fe^+ , FeCO^+
221	$\text{C}_{10}\text{H}_{21}\text{O}_5^+$	$\text{C}_6\text{H}_{13}\text{O}_3^+$

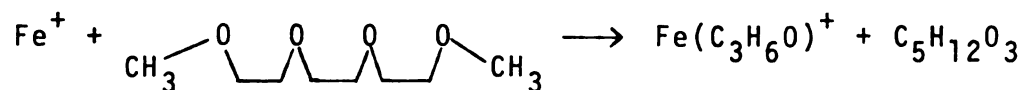
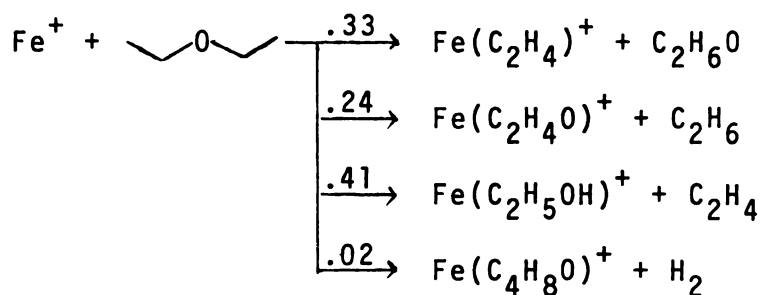
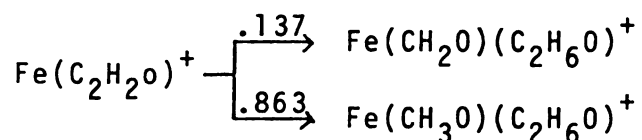
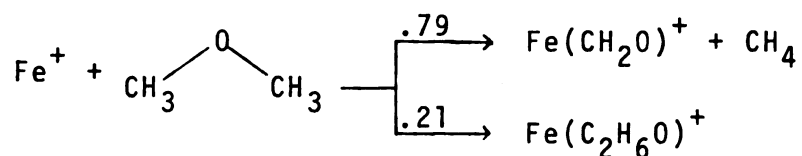
<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
242	$\text{FeCO}(\text{C}_8\text{H}_{14}\text{O}_3)^+$	FeCO^+ , $\text{Fe}(\text{CO})_2^+$
248	$\text{Fe}(\text{C}_8\text{H}_{16}\text{O}_5)^+$	$\text{Fe}(\text{CO})_2^+$
276	$\text{FeCO}(\text{C}_8\text{H}_{16}\text{O}_5)^+$	$\text{Fe}(\text{CO})_3^+$

B. Discussion

1. Linear Ethers and Polyethers

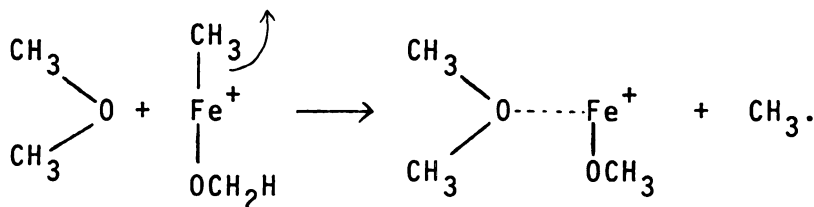
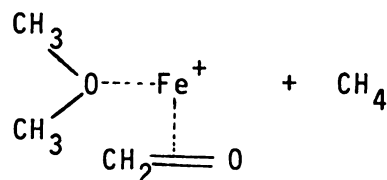
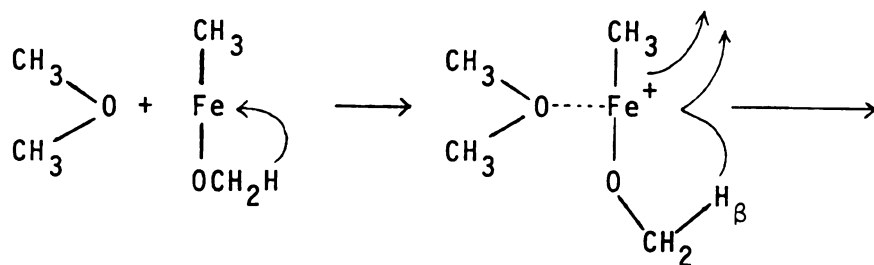
a. Reactions of Fe^+

The Fe^+ reactions with dimethyl ether, diethyl ether and TDE are summarized below:



Basically, all these reaction products can be explained in terms of Scheme X, i.e. Fe^+ inserts into a C—O bond,

The successive reaction products, $\text{Fe}(\text{CH}_2\text{O})(\text{C}_2\text{H}_6\text{O})^+$ and $\text{Fe}(\text{CH}_3\text{O})(\text{C}_2\text{H}_6\text{O})^+$ in the reaction of Fe^+ with dimethyl ether can be explained as follows:



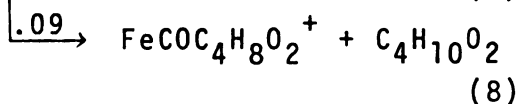
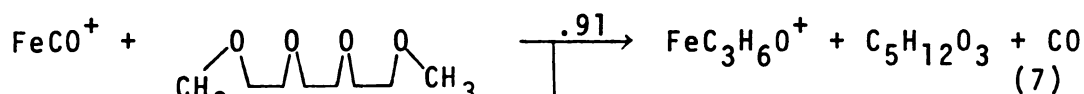
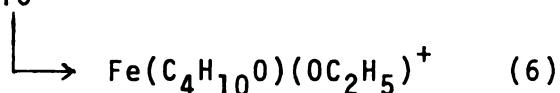
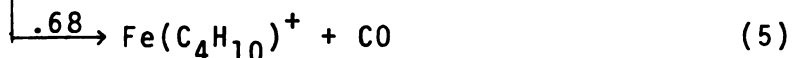
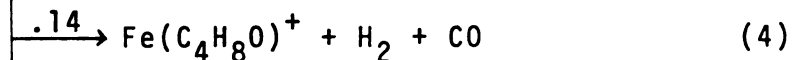
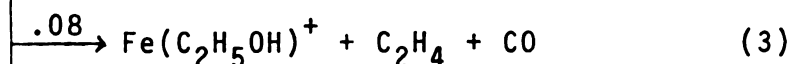
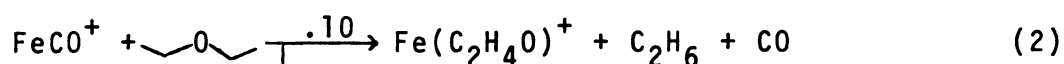
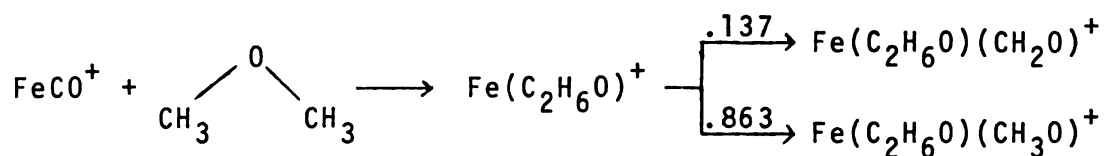
That is, the real structure of $\text{Fe}(\text{C}_2\text{H}_6\text{O})^+$ is that in which Fe^+ has inserted into the C-O bond. When another molecule approaches, a β -H shifts to eliminate CH_4 . Alternatively, the incoming dimethyl ether can undergo substitution to replace the CH_3 group.

Note that the Fe^+ reaction with TDE only produces one product ion, $\text{FeC}_3\text{H}_6\text{O}^+$. When the reactant neutral becomes a polyether, multiple metal-ligand interactions are expected, since these are observed in solution. While the number of

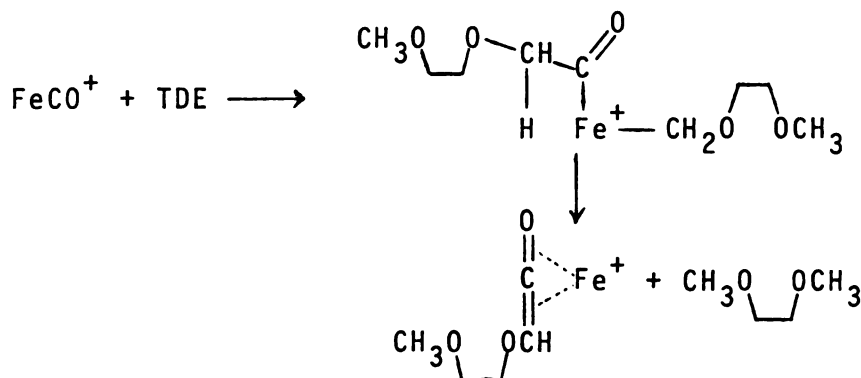
atoms in TDE with which the metal ion initially interacts may be > 1 , the actual reactions occur involving only one site on the polyether. The initial multiple interaction may be important in directing the metal to a site of attack (insertion). The mechanism proposed above is typical in that, when the metal ion rearranges TDE into two smaller molecules, the smaller one is usually retained as a ligand, presumably being due to its effective electron donating ability of the smaller ligands.

b. Reactions of FeCO^+

FeCO^+ reactions with dimethylether, dimethylether and TDE are summarized below:



The processes in (1)-(4) were observed for Fe^+ alone and are presumed to occur by the same mechanism, however here we have concurrent cleavage of the $\text{M}-\text{CO}^+$ bond. Reaction (5) is a commonly observed ligand substitution. Reaction (6) is similar to (2) where an alkoxy group replaces an alkyl group. $\text{FeC}_3\text{H}_6\text{O}^+$ in reaction (7) was also formed by Fe^+ alone as explained in the last section. In reaction (8), since (a) $\text{C}_4\text{H}_8\text{O}_2$ is not "extracted" from TDE by Fe^+ alone, and (b) the CO is retained, we interpret this as a MCO^+ insertion into the center of the molecule, followed by a β -H shift.



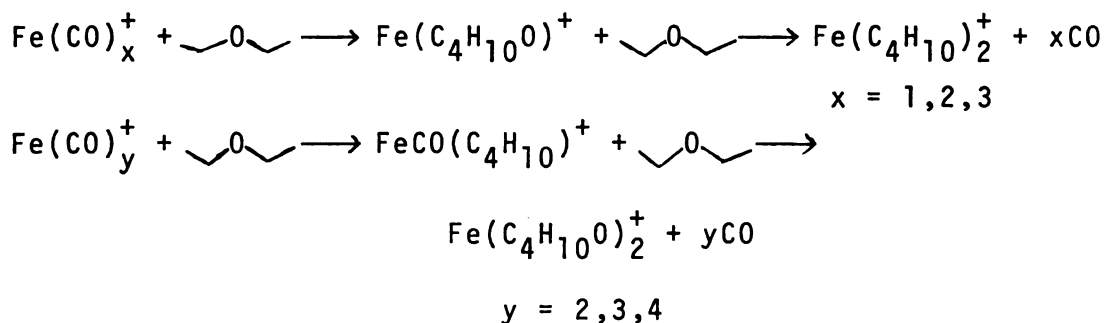
Note that, without incorporation of CO in the intermediate, no β -H atoms would be available to shift. The product resembles a metal-ketene complex, which is frequently observed in such studies⁹¹.

c. Reactions of other $\text{Fe}(\text{CO})_x^+$ ions

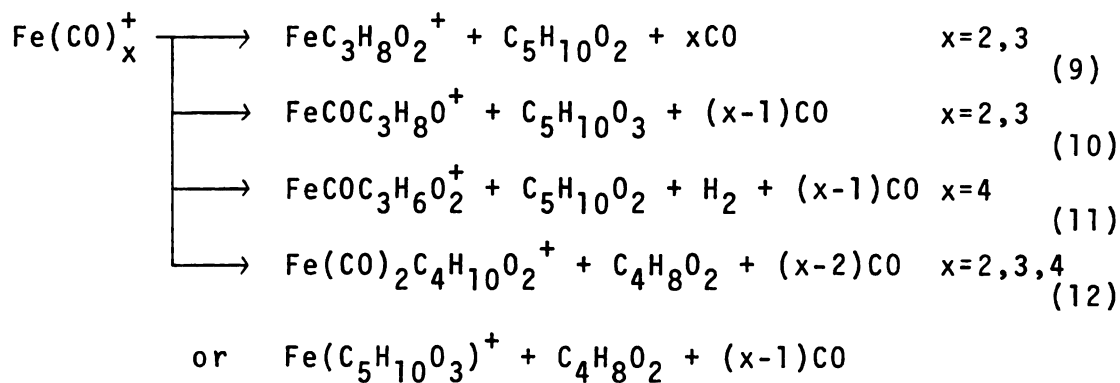
As indicated in the reaction product lists, as the number of CO's present on the metal increases, ligand substitution becomes the predominant process. $\text{Fe}(\text{CO})_2^+$ and $\text{Fe}(\text{CO})_3^+$

will react with dimethylether to form $\text{FeCO}(\text{C}_2\text{H}_6\text{O})^+$ with loss of up to 2 CO's. Diethylether can displace up to 3 CO's and so on, which is typical of other systems studied⁸⁵ - in fact most compounds which have been studied except alkyl fluorides^{92,122} have been observed to displace CO from charged transition metal centers.

Successive reactions also become important at higher pressures, for example:

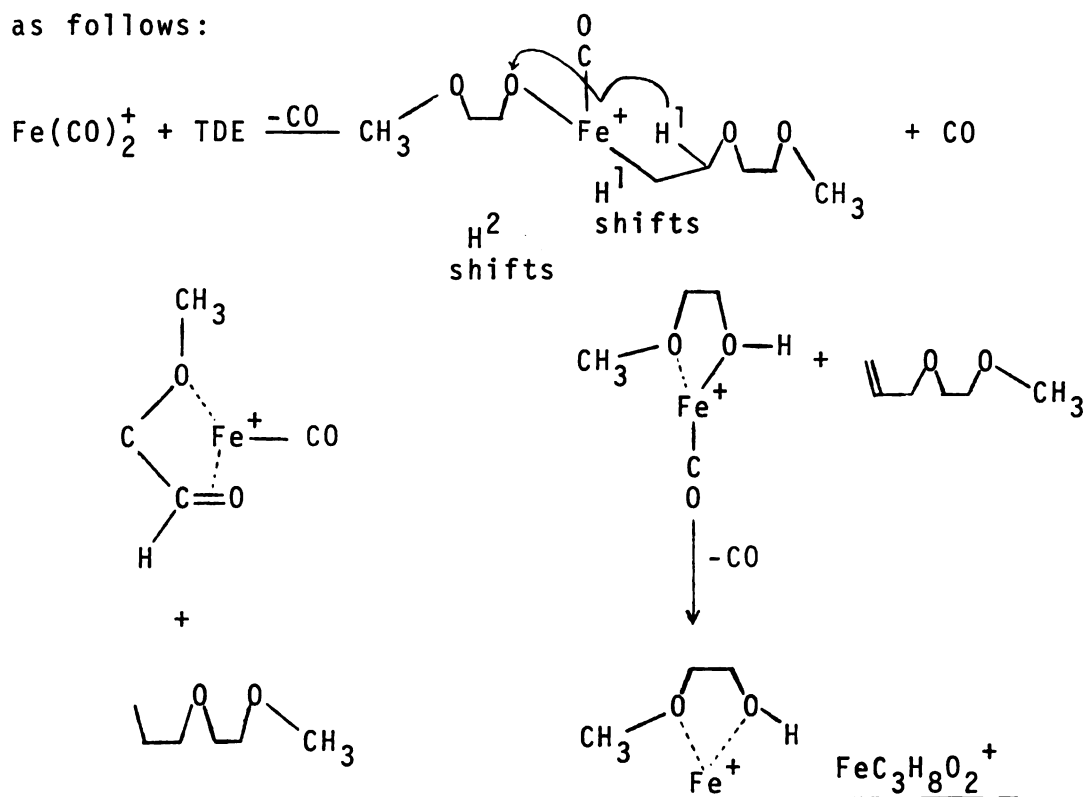


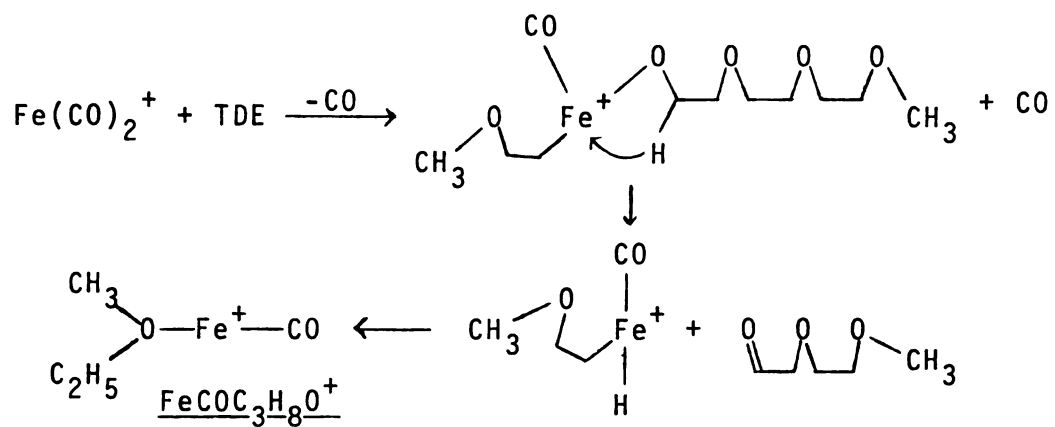
However, in these studies, no ion of composition $\text{Fe}(\text{TDE})^+$ was observed. The reactions of $\text{Fe}(\text{CO})_x^+$ with TDE are summarized below:



All of the products for TDE are reactive rearrangements of the TDE; none are CO displacement. This may reflect the ability of TDE to complex stepwise with the metal center i.e.- initial complexation may involve one oxygen of the ligand. As further oxygens interact, additional energy is made available for metal-induced decomposition of the polyether.

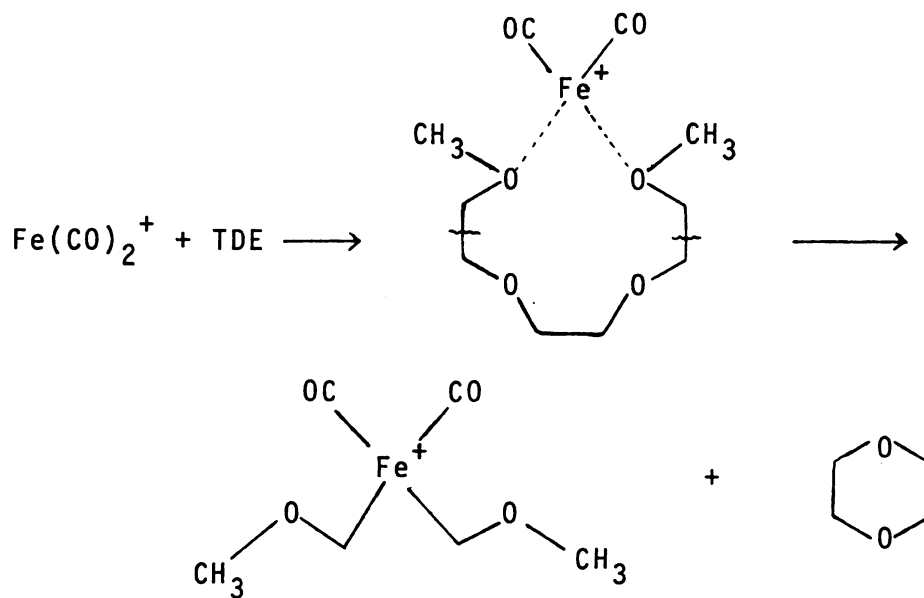
Hence reactions (9), (10) and (11) can be explained as follows:



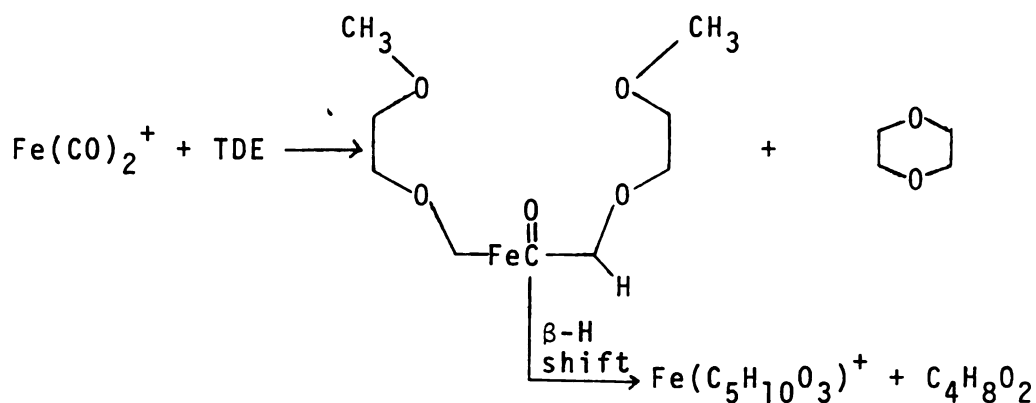


Note that the reactivity (which will be defined here as the number of products) increases as the neutral changes from an ether to a polyether. Also note that the CO ligands can be lost in a stepwise manner.

The formation of $\text{Fe(CO)}_2\text{C}_4\text{H}_{10}\text{O}_2^+$ is very difficult to explain, however, the following mechanisms are possible.



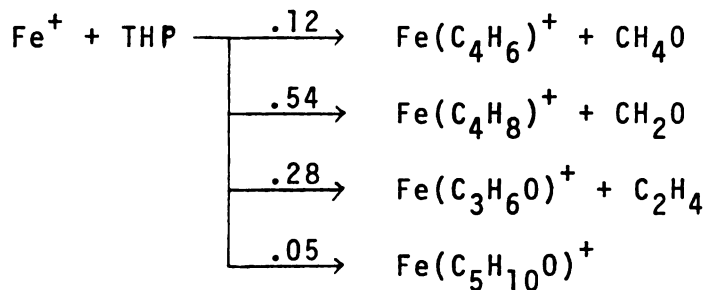
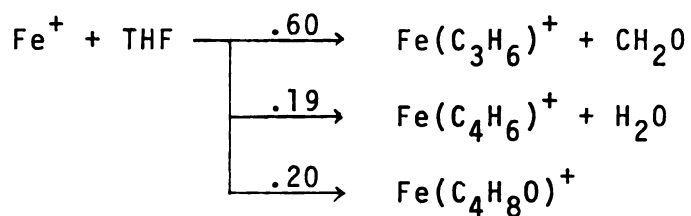
or



2. Cyclic Ethers

a. Fe^+ reactions with THF and THP.

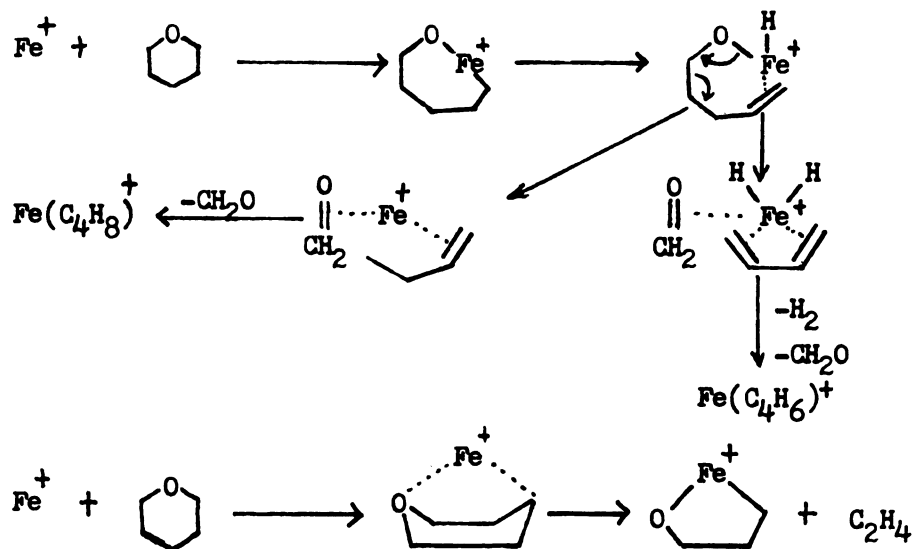
Fe^+ reactions with tetrahydrofuran and tetrahydropyran are summarized below:



Again, all the products can be explained in terms of a metal insertion followed by a β -shift. The reaction mechanism of Fe^+ with THP is shown as an example in Scheme XI.

(The reaction mechanisms for Fe^+ with THF is shown in Scheme II)

Scheme XI.



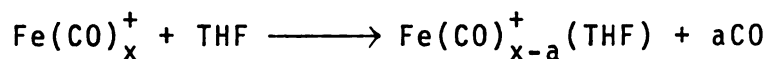
Note that in the THF reactions, the formation of an intermediate containing C_3H_5 is a strong driving force. In THP, there is no favorable mechanism for forming this intermediate. Fe^+ does react with THP to form $\text{Fe}(\text{C}_3\text{H}_6\text{O})^+$, which is reasonable, being geometrically accessible (5-membered ring) and that Fe^+ interacts with both oxygen and carbon equally well. (Table 2 p.20).

b. $\text{Fe}(\text{CO})_x^+$ reactions with THF and THP

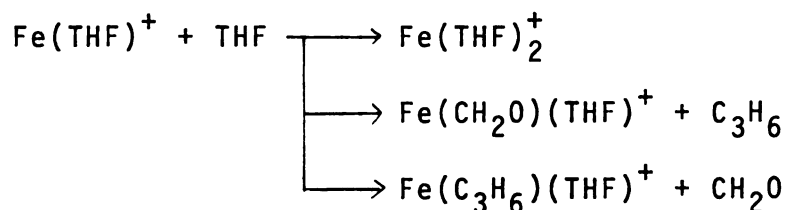
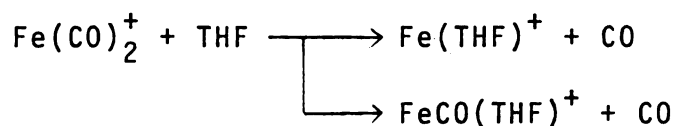
Usually, the more ligands on the metal center, the less reactive these species will be except in the reaction with multifunctional organic compounds as explained in the last section. Hence in the reactions of $\text{Fe}(\text{CO})_x^+$ with THF and THP,

we only see the same products as Fe^+ formed (by the same mechanism presumably) with concurrent cleavage of the M^+-CO bond.

Ligand substitution and successive reactions also become important such as:



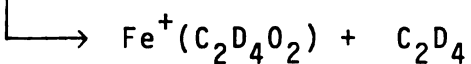
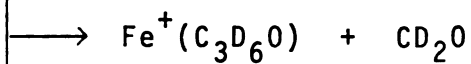
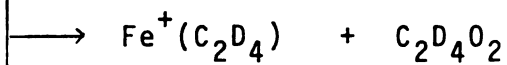
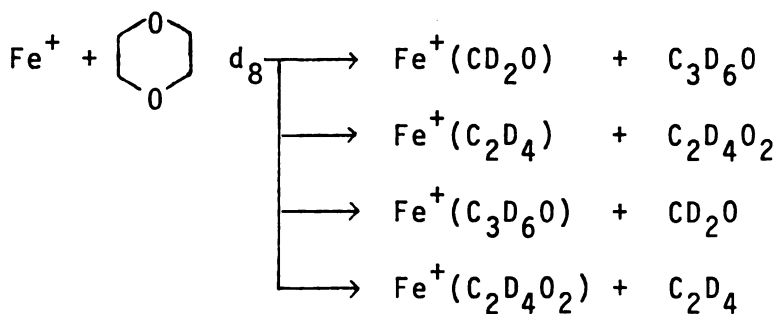
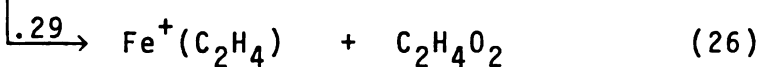
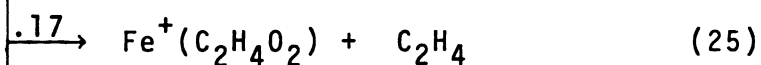
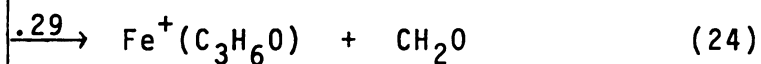
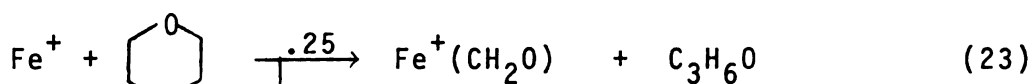
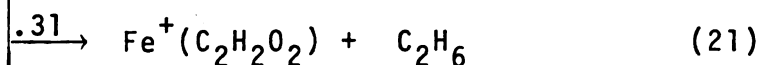
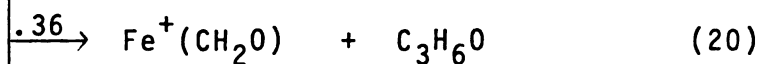
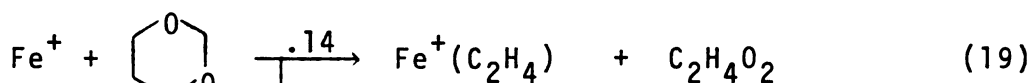
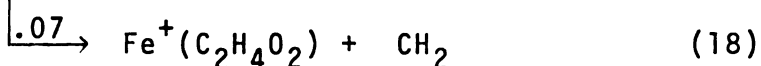
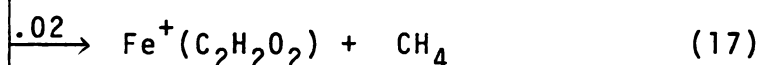
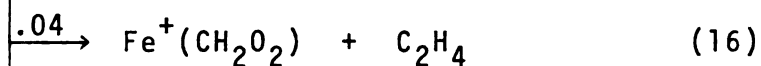
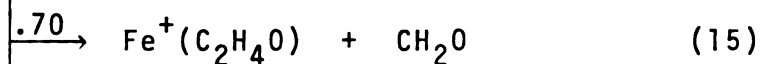
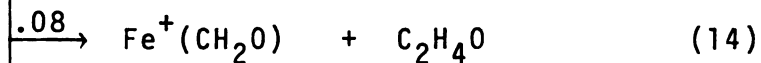
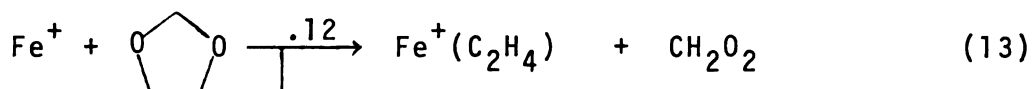
```
for x = 2 a = 1
```

$$x = 3 \qquad a = 2$$
$$x = 4 \quad a = 2,1$$
$$x = 5 \quad a = 2,1$$


3. Cyclic Polyethers

a. Fe⁺ reactions with 1,3 dioxolan,
1,3 dioxane, p-dioxane-(d₈),
12-crown-4 and 15-crown-5

Fe⁺ reactions with 1,3 dioxolan, 1,3 dioxane, p-dioxane (d₈), 12-crown-4 and 15-crown-5 are summarized below and in Table 5.



In its reactions with monofunctional ethers, both acyclic and cyclic ethers, it is energetically favorable for Fe^+ to insert into the C-O bond, followed by a β -H shift. If Fe^+ interacts with two geometrically accessible oxygens which are in close proximity, such an interaction may involve more than twice the energy as the interaction with only one oxygen due to the ligand effect¹²⁴. This may result in a double insertion and double β -shift mechanism. This process can be stepwise¹⁴⁵, although it is convenient to use a concerted double insertion, followed by double β -H shifts (using a stepwise mechanism, it is hard to explain reactions (17) and (18)). Accordingly, the products in reactions (13)-(18) can be explained as follows:

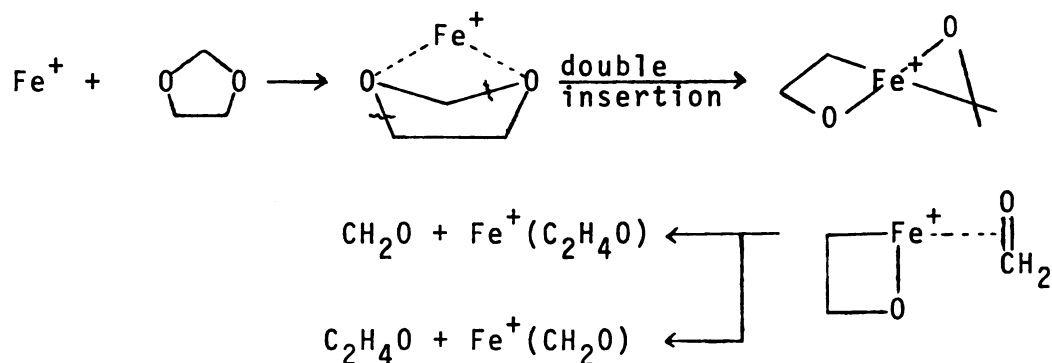
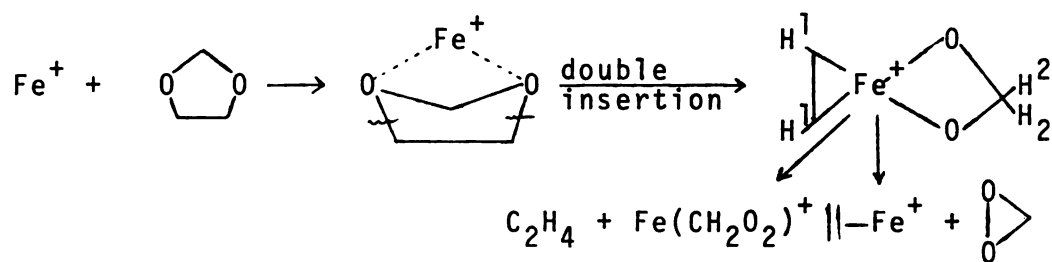
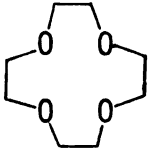
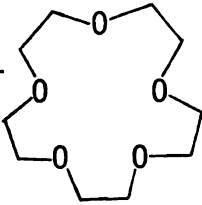
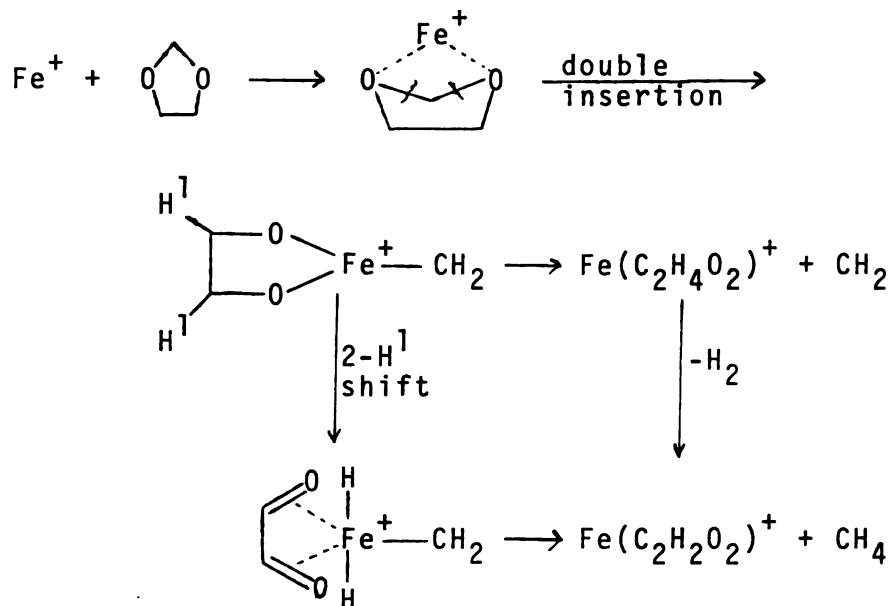


Table 5. Ion/Molecule Reactions of Fe^+ With 12-crown-4
And 15-crown-5.

		See Scheme
$\text{Fe}^+ + $ 	$\xrightarrow{.22} \text{Fe}^+ \text{C}_2\text{H}_2\text{O} + \text{C}_6\text{H}_{12}\text{O}_3 + \text{H}_2\text{O}$	XII
	$\xrightarrow{.13} \text{Fe}^+ \text{C}_2\text{H}_2\text{O}_2 + \text{C}_6\text{H}_{14}\text{O}_2$	XIII
	$\xrightarrow{.41} \text{Fe}^+ \text{C}_2\text{H}_4\text{O}_2 + \text{C}_6\text{H}_{12}\text{O}_2$	XIII
	$\xrightarrow{.02} \text{Fe}^+ \text{C}_4\text{H}_4\text{O} + \text{C}_4\text{H}_{10}\text{O}_3 + \text{H}_2$	XIV
	$\xrightarrow{.01} \text{Fe}^+ \text{C}_4\text{H}_6\text{O} + \text{C}_4\text{H}_{10}\text{O}_3$	XIV
	$\xrightarrow{.12} \text{Fe}^+ \text{C}_4\text{H}_8\text{O}_2 + \text{C}_4\text{H}_8\text{O}_2$	XII
	$\xrightarrow{.06} \text{Fe}^+ \text{C}_4\text{H}_{10}\text{O} + \text{C}_4\text{H}_6\text{O}_3$	XIV
	or $\text{Fe}^+ \text{C}_3\text{H}_6\text{O}_2 + \text{C}_5\text{H}_{10}\text{O}_2$	
	$\xrightarrow{.01} \text{Fe}^+ \text{C}_4\text{H}_8\text{O}_3 + \text{C}_4\text{H}_8\text{O}$	XIV
	$\xrightarrow{.02} \text{Fe}^+ \text{C}_6\text{H}_{14}\text{O}_2 + \text{C}_2\text{H}_2\text{O}_2$	XIII
$\text{Fe}^+ + $ 	$\xrightarrow{.05} \text{Fe}^+ (\text{C}_2\text{H}_2\text{O}_2) + \text{C}_8\text{H}_{16}\text{O}_3 + \text{H}_2$	XV
	$\xrightarrow{.20} \text{Fe}^+ (\text{C}_2\text{H}_4\text{O}_2) + \text{C}_8\text{H}_{16}\text{O}_3$	XV
	$\xrightarrow{.26} \text{Fe}^+ (\text{C}_2\text{H}_6\text{O}) + \text{C}_8\text{H}_{14}\text{O}_4$	XV, XVI
	$\xrightarrow{.11} \text{Fe}^+ (\text{C}_4\text{H}_8\text{O}_2) + \text{C}_6\text{H}_{12}\text{O}_3$	XVII
	$\xrightarrow{.12} \text{Fe}^+ (\text{C}_6\text{H}_{14}\text{O}_2) + \text{C}_4\text{H}_6\text{O}_3$	XVIII
	$\xrightarrow{.21} \text{Fe}^+ (\text{C}_4\text{H}_8\text{O}_3) + \text{C}_6\text{H}_{12}\text{O}_2$	XVIII
	$\xrightarrow{.05} \text{Fe}^+ (\text{C}_8\text{H}_{14}\text{O}_3) + \text{C}_2\text{H}_6\text{O}_2$	XV

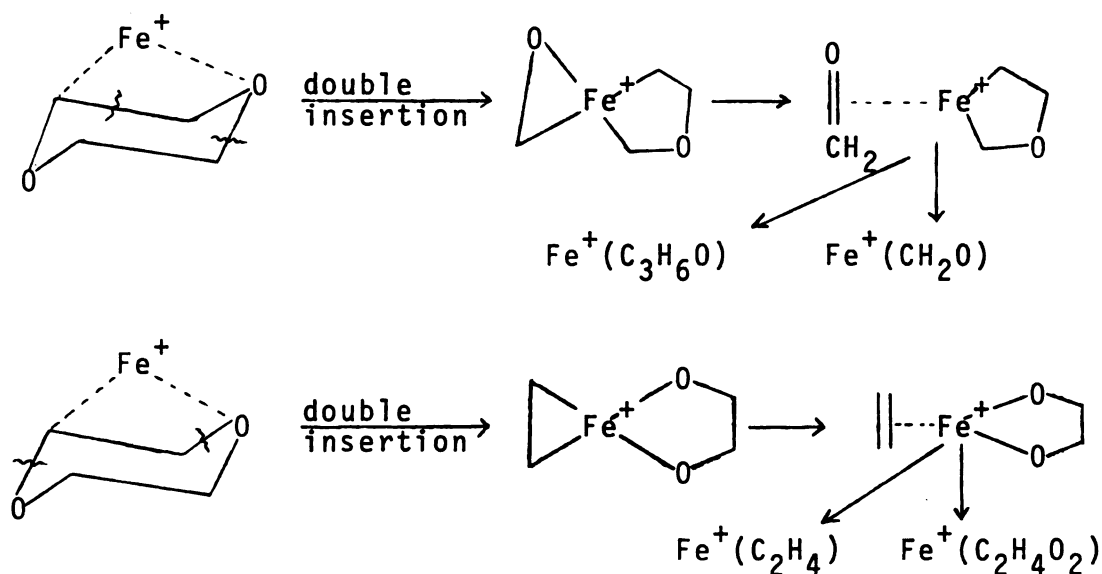


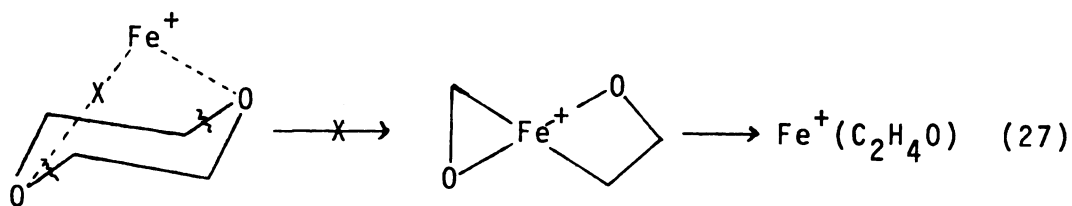
Note that there are only three possibilities for double insertion, each case gives the corresponding products.

Reactions (23)-(26) were identified unambiguously by p-dioxane d_8 reactions. The product ion in reaction (21) can be either $\text{Fe}(\text{C}_2\text{H}_2\text{O}_2)^+$ or $\text{Fe}(\text{C}_3\text{H}_6\text{O})^+$. $\text{Fe}(\text{C}_3\text{H}_6\text{O})^+$ is more reasonable based on the p-dioxane reactions (23)-(26) and can be easily explained by the proposed mechanism which follows.

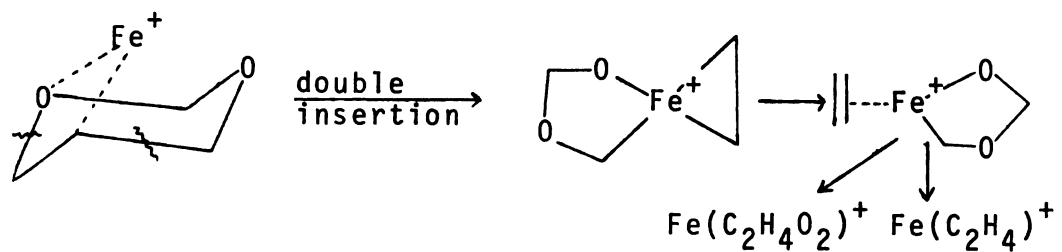
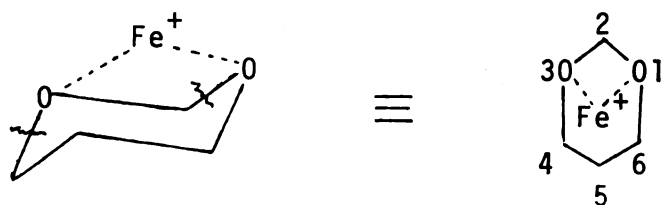
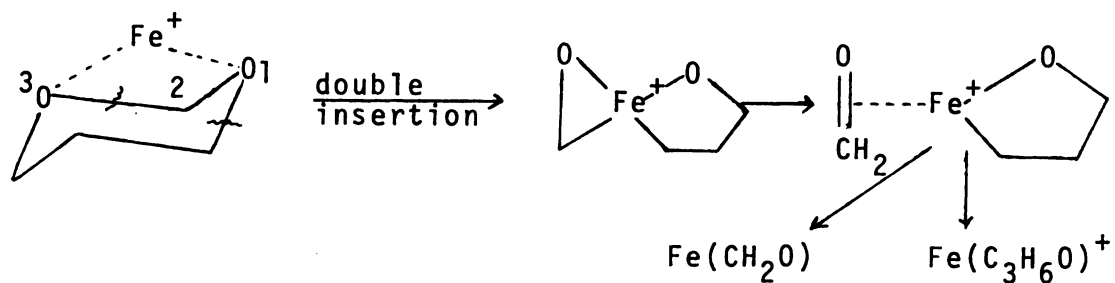
Note that the chair form of p-dioxane is the most stable conformation based on electron diffraction, sector microphotometer studies^{125,126}, and complexation¹²⁷⁻¹²⁹ studies. It is shown that $\angle\text{COC}$ of p-dioxane is 112.45° which is bigger than that of cyclohexane (108°)¹²⁶. Therefore we assume that it is the most stable conformer in the gas phase. From X-ray studies of 2-chlorophenyl-1,3

dioxane¹³⁰ and conformational analysis^{131,132} and modeling studies¹³¹, it is agreed that 1,3 dioxane is more stable in the chair form with the $\angle O_1C_3O_3 = 111^\circ$, which is puckered (dihedral angle, $\tau = 63^\circ$) and $\angle C_4C_5C_6 = 108^\circ$, which is flattened (dihedral angle, $\tau = 55^\circ$), although the under-derivatized ligand has not been studied. Since Fe^+ has almost the same bonding energy to oxygen and to an alkyl group (Table 2) and because of the geometrical accessibility, Fe^+ is capable of interacting with both oxygens and one carbon as indicated by dashed lines in the following mechanisms. However, it appears that Fe^+ is even more likely to interact with one oxygen and one carbon instead of two oxygens due to the geometrical restriction. The products in reactions (19)-(26) can then be explained by the "double insertion, double β -H shift" mechanism, as shown below:

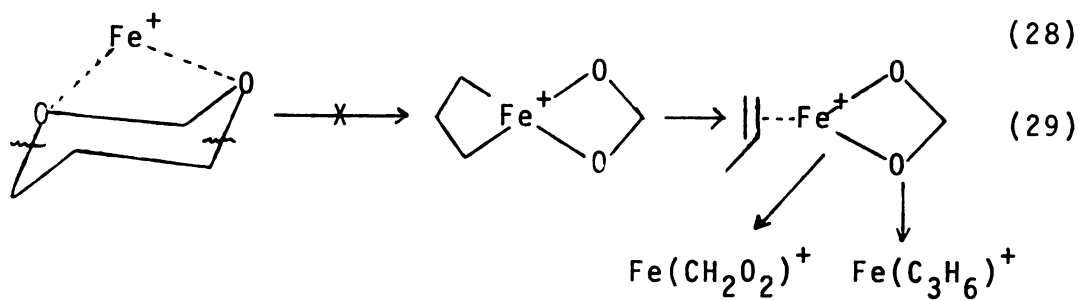




Similarly,



(28)



(29)

Note that the only reason why reaction (27) doesn't occur is because Fe^+ can't interact with two oxygens and one $-\text{CH}_2-$ group at the same time. It is difficult for Fe^+ to interact with two separated oxygens by breaking bonds as shown in (27). Instead, it prefers to interact with one oxygen and one methylene group. In the case of 1,3-dioxane, Fe^+ can either interact with two oxygens or one oxygen and one $-\text{CH}_2-$ group equally well. Since the $\text{O}_3-\text{C}_4-\text{C}_5$ angle is flattened¹³⁰, the $-\text{CH}_2-$ at C_5 can have a weak interaction with Fe^+ unless Fe^+ moves closer and weakens its interaction with another oxygen as in reaction (28). The reason why reaction (29) doesn't occur is probably because the O_1-C_2 and C_2-O_3 bonds become weaker than other bonds, due to the strong interaction of Fe^+ with two oxygens, which forms a strained four membered ring intermediate and results in an insufficient orbital overlap of O_1-C_2 and C_2-O_3 bonds, in contrast with more flexibility of $\text{O}_1\text{C}_6\text{C}_5\text{C}_4\text{O}_3$ ring on the other side. Therefore, O_1-C_2 and C_2-O_3 bonds are easier to break and C_6-O_1 and O_3-C_4 are more resistive to cleavage.

Also note that all of the products in the reactions of Fe^+ with 1,3 dioxane and 1,4-dioxane are from the metal ion "double insertion" only, because β -H's may not be geometrically accessible for shifting after double insertion by the Fe^+ , which might have a linear structure for the intermediate, $\text{RCH}_2-\text{Fe}^+-\text{OR}$. Linear structures for insertion products have been suggested by D.P. Ridge in the reactions

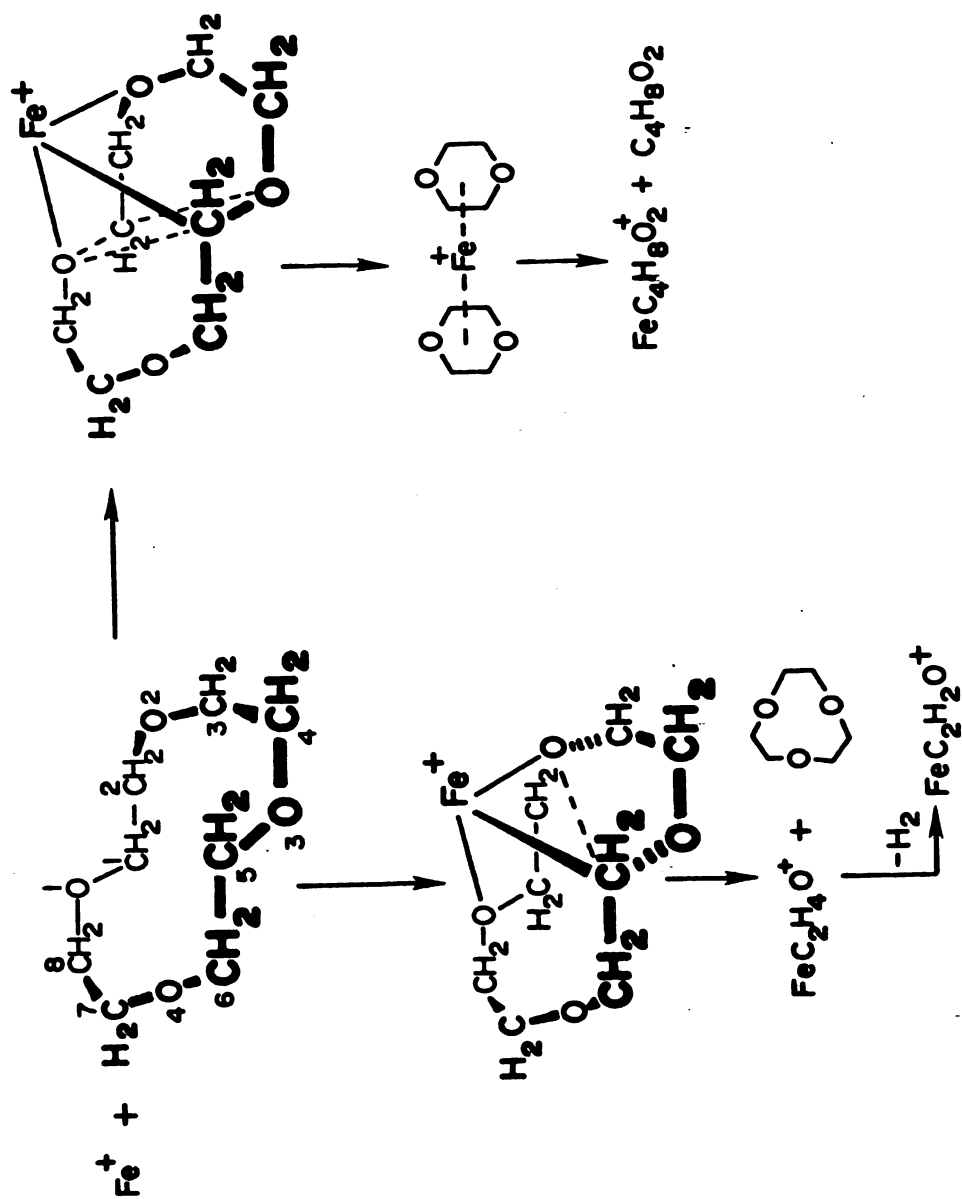
of Fe^+ with alkanes¹⁹⁴.

In 12-crown-4, the chemistry is even richer. The reaction products together with their reaction mechanisms are indicated in Table 5.

In some cases, Fe^+ appears to break down the polyether into smaller cyclic ethers, which is also observed on electron impact of crown ethers¹³³. One product, $\text{FeC}_4\text{H}_8\text{O}_2^+$, appears to be the result of cleavage of 12-crown-4 into two 1,4-dioxane molecules which is shown in Scheme XII. The process is favored since 2 molecules of 1,4-dioxane are approximately 20 kcal/mole more stable than 1 molecule of 12-crown-4¹³⁴.

This arrangement of 12-crown-4 is consistent with a distinct secondary structure for the polyether which is shown in Scheme XII. This structure was derived from X-ray crystallographic studies¹³⁶. Thus, we assume that it may also be a favored configuration for the uncomplexed crown in the gas phase. (While the molecule is free to assume many secondary structures, intramolecular hydrogen bonding may favor this configuration^{107,111}.) Using the numbering system of Scheme XII, it can be seen that this chair-type structure has two oxygen atoms whose lone pairs are directed above the "plane" of the molecule (1 and 2) and two below (3 and 4). If Fe^+ can complex with this ligand without extensive changes in the secondary structure, initial complexation with lone pairs on oxygen atom #1 and #2 will

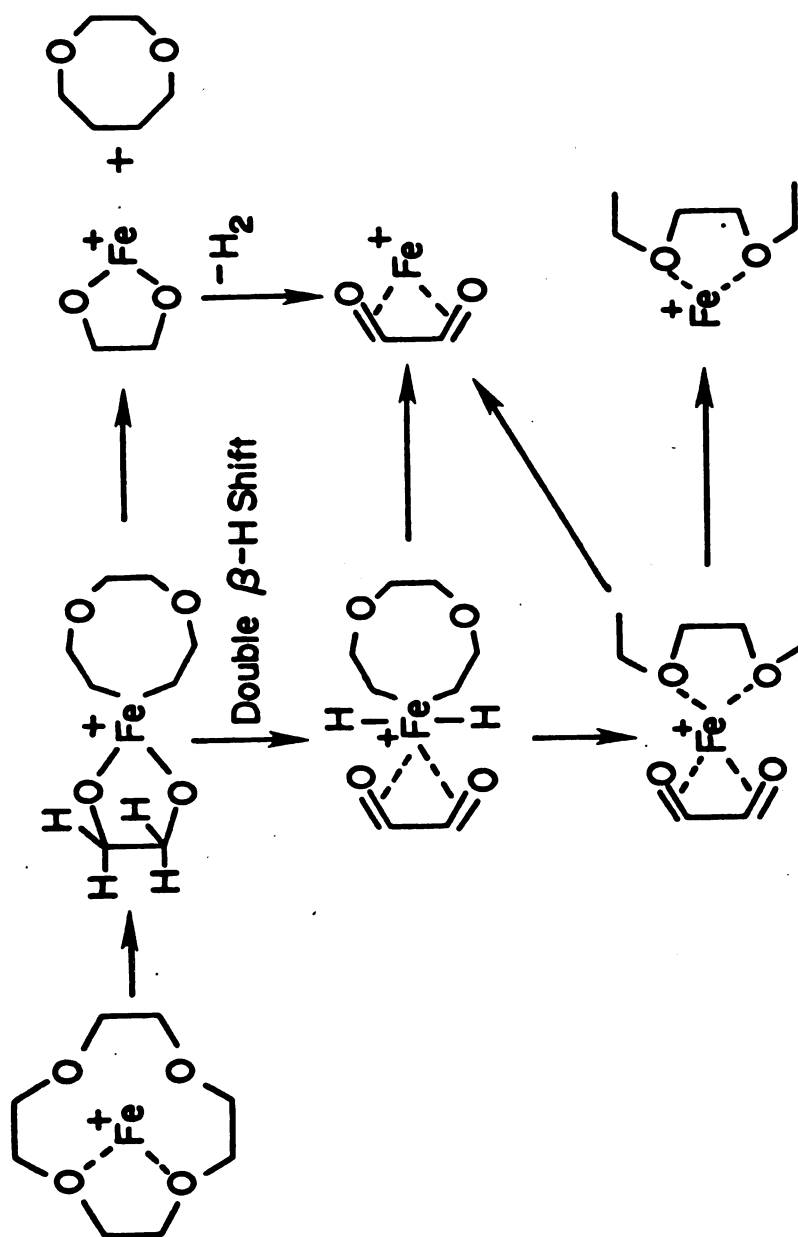
SCHEME XII



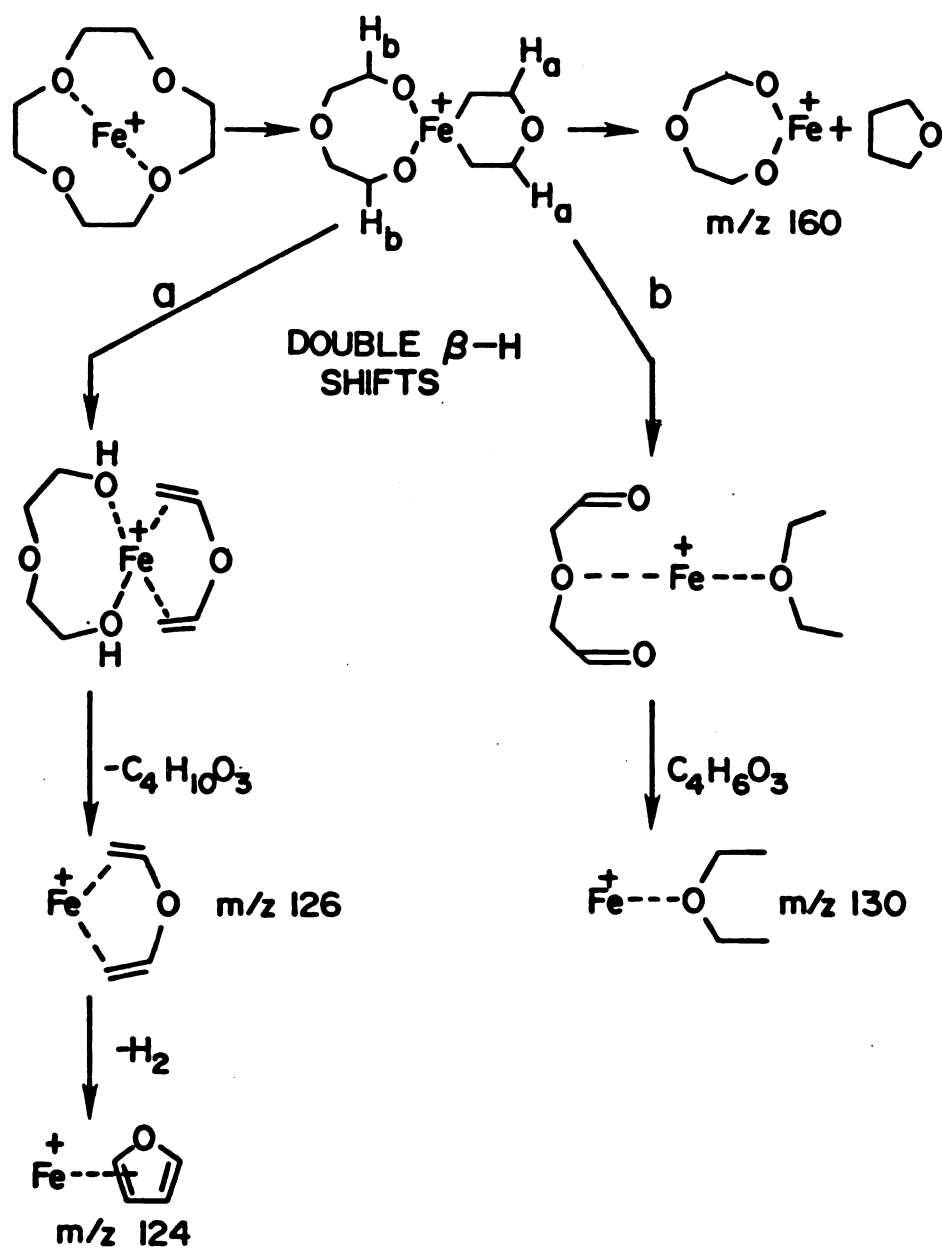
direct the metal towards C #5. These three atoms are in close proximity in this model. Scheme XII shows that such an initial interaction would lead to the $\text{FeC}_4\text{H}_8\text{O}_2^+$ product if Fe^+ can bring O#1 and C#5 in close proximity to form two rings (two p-dioxanes). On the other hand, if this interaction brings C#5 and O#2 in closer proximity, 9-crown-3 can be eliminated, leaving $\text{FeC}_2\text{H}_4\text{O}^+$ which rapidly loses H_2 to form $\text{FeC}_2\text{H}_2\text{O}^+$, which is also observed. Thus, the geometry of "free" 12-crown-4 suggests that, regardless of which side of the ring Fe^+ attacks, there will be two O atoms and one CH_2 unit (which is across the ring) in close proximity for initial interaction with the metal, similar to the cases of 1,3-dioxane and 1,4-dioxane which have been discussed earlier. The geometry may facilitate the formation of new C-O bonds and smaller rings.

Other products can be explained following initial metal complexation to the two oxygen atoms shown in Scheme XIII and XIV followed by metal ion double insertion and double β -H shifts as previously discussed. There are only two possibilities. Fe^+ can interact with either two oxygen atoms next to each other or two oxygen atoms across the ring. Scheme XIII shows the former case to form $\text{FeC}_2\text{H}_4\text{O}_2^+$, $\text{FeC}_2\text{H}_2\text{O}_2^+$ (similar to a metal-butadiene complex) and $\text{FeC}_6\text{H}_{14}\text{O}_2^+$. Note that it also follows initial interaction with oxygen atoms #1 and #2. Following the double insertion, we see a situation where both the "left" and "right" groups

SCHEME XIII

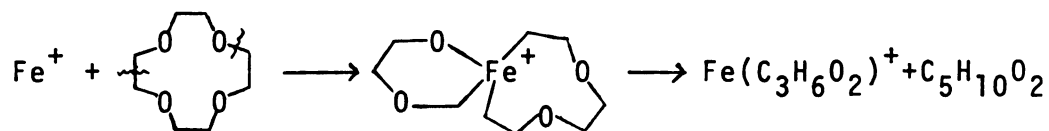


SCHEME XIV



contain β -H atoms which could shift. Apparently, only those on the "left" do. Molecular models suggest that further interaction of the oxygens on the "right" group with the metal ion may move the "right" β -H atoms to positions spatially less accessible. These additional metal-oxygen interactions could thus, through an intermediate such as is shown in Fig. 8, control the availability of β -H atoms for rearrangement.

Scheme XIV predicts the remainder of the products through another double insertion, double β -H shift scheme, following an initial complexation of Fe^+ with two oxygen atoms across ring. Note that if H's from the "left" shift, $\text{FeC}_4\text{H}_{10}\text{O}^+$ is formed, which corresponds to an ion of m/e 130. An alternative structure ($\text{FeC}_3\text{H}_6\text{O}_2^+$) for the same ion can be explained by a double insertion:



Here, Fe^+ interacts preferentially with oxygen atom #1 and carbon atom #5 as indicated in Scheme XII and inserts into both the C-C and the C-O bonds similar to reaction (28). Nevertheless, CID or high resolution spectra are required to unambiguously distinguish $\text{FeC}_4\text{H}_{10}\text{O}^+$ from $\text{FeC}_3\text{H}_6\text{O}_2^+$.

In the reaction of Fe^+ with 15-crown-5, one may expect to get more products, presumably due to increased interaction

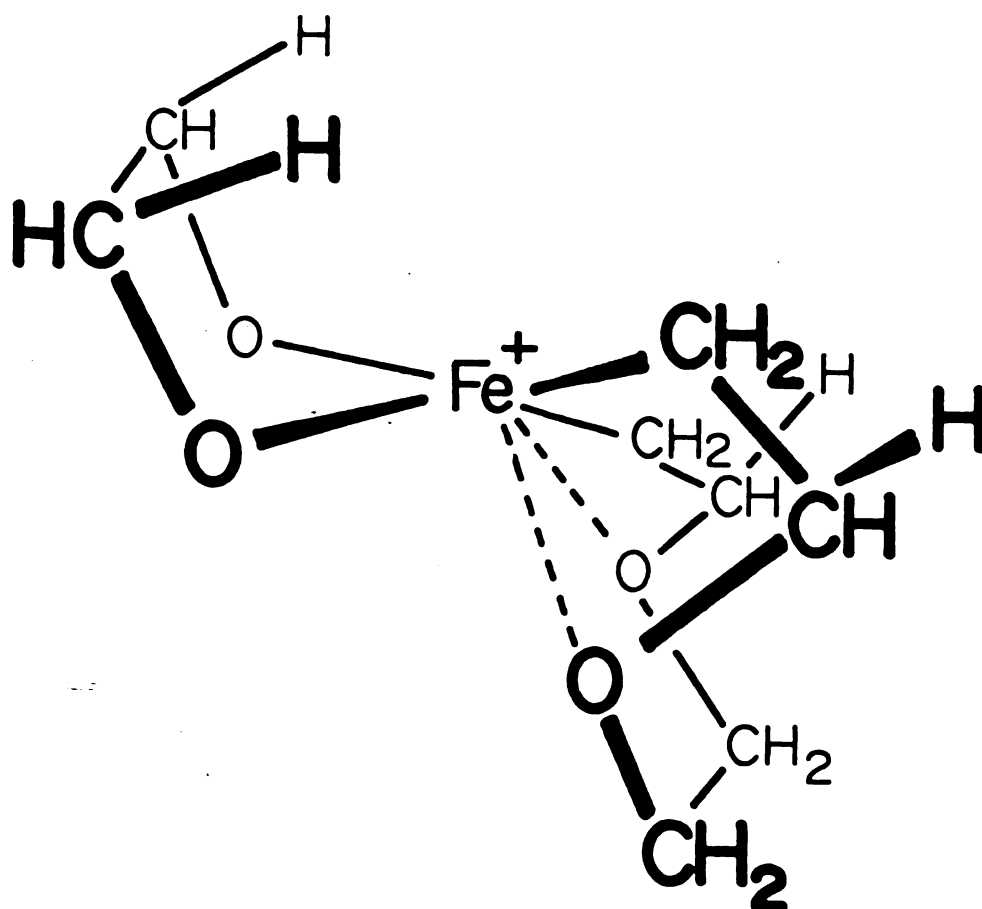


Figure 8. A Structure Of Fe^+ -12-crown-4 After Fe^+ Double Inserts Into Two C-O Bonds Of 12-crown-4

of Fe^+ with five oxygen atoms in 15-crown-5. However, Fe^+ apparently can't react effectively with all 5 oxygens. (15-crown-5 has much bigger cavity than 12-crown-4 does ($1.7 - 2.2 \text{ \AA}$ vs. $1.2 - 1.5 \text{ \AA}$ in diameter)).

Although there are many reports on the complexed structures of 18-crown-6¹³⁷ and also its free ligand¹³⁸, there are only a few reports on complexed 15-crown-5^{112,139,140} and the study of the free 15-crown-5 molecule has not been reported yet. However, the structure of 15-crown-5 was taken by X-ray and drawn in reference 139, in which the copper in CuBr_2 interacts with only one oxygen atom of 15-crown-5, which makes the conformation of 15-crown-5 similar to that of a free ligand as shown in Fig. 9.

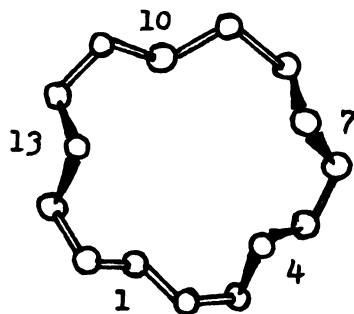
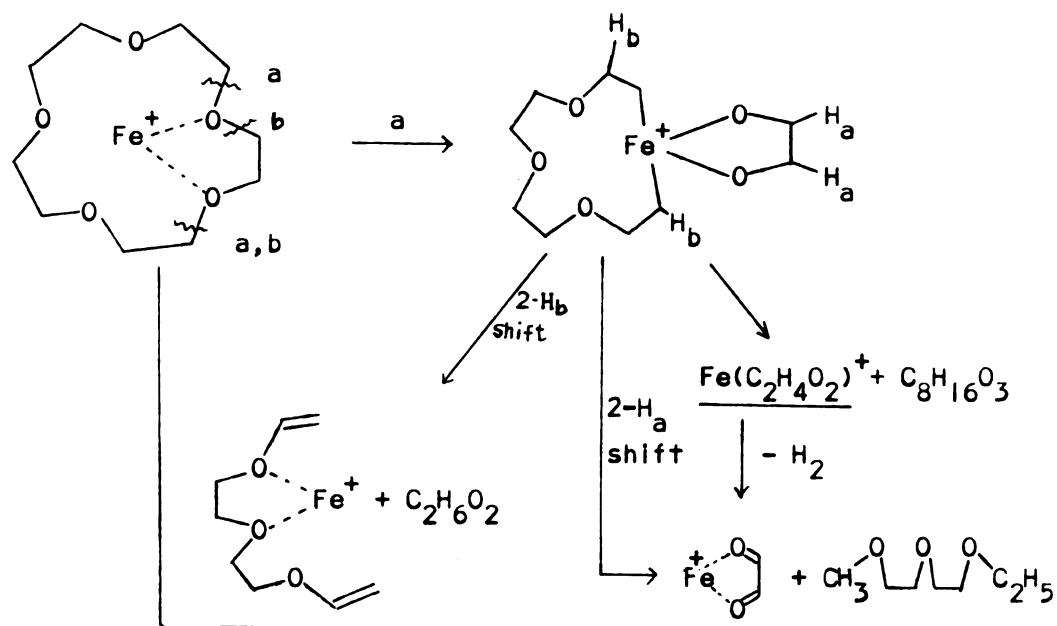


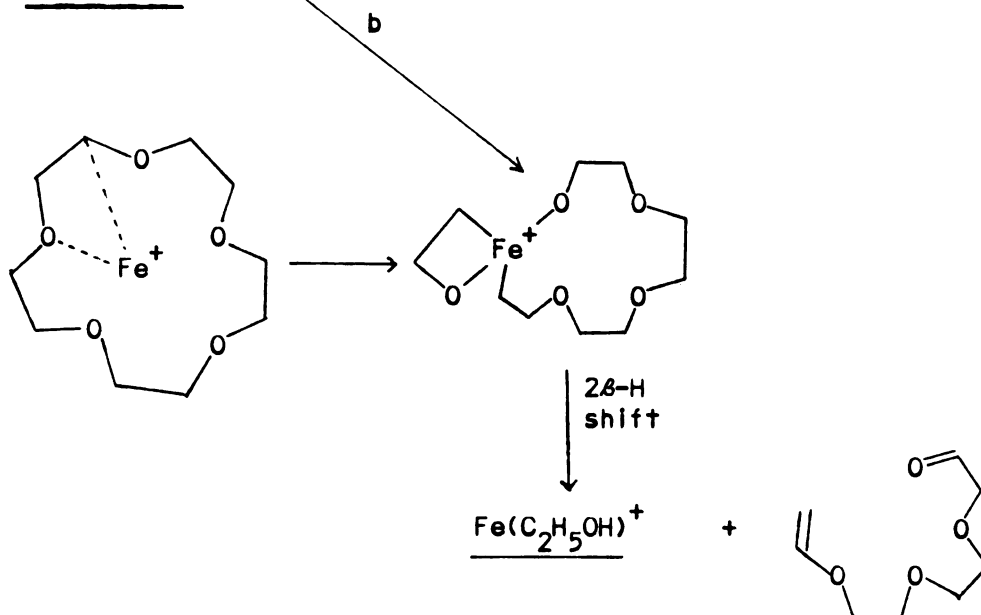
Figure 9

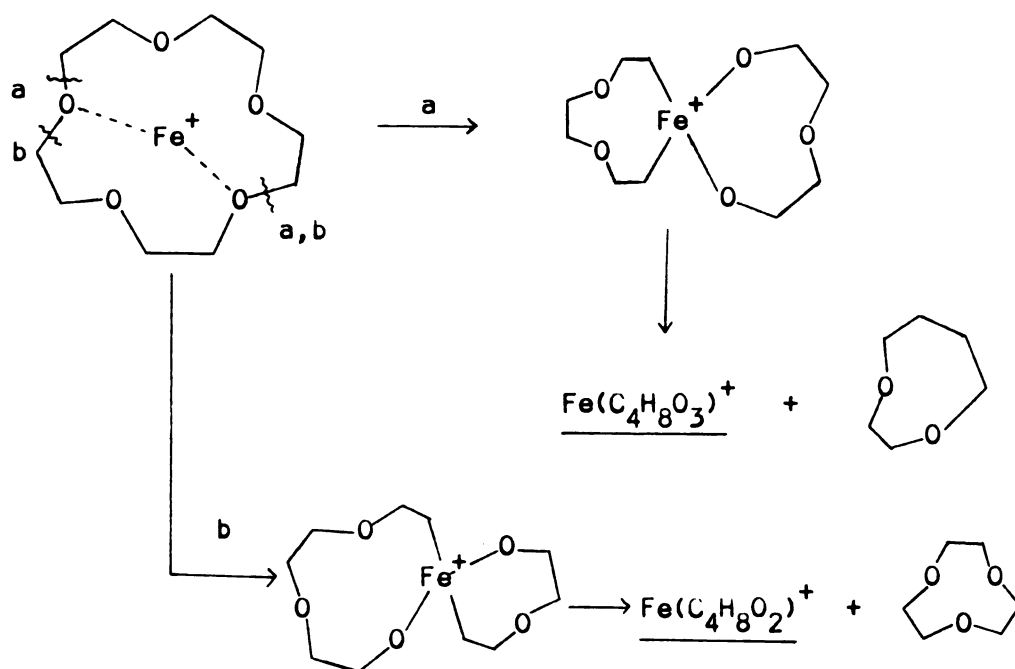
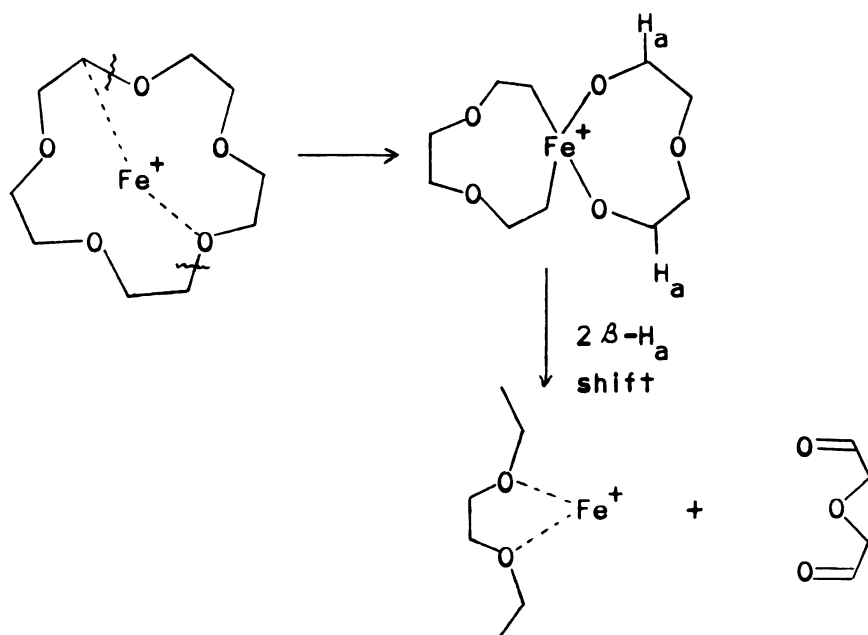
X-Ray Structure Of 15-Crown-5
In 15-Crown-5 CuBr_2 .

Scheme XV

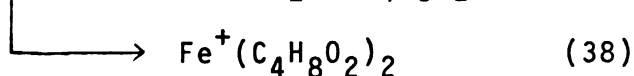


Scheme XVI



Scheme XVIIScheme XVIII

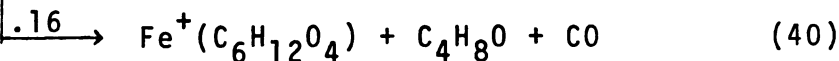
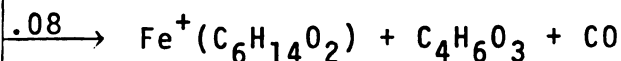
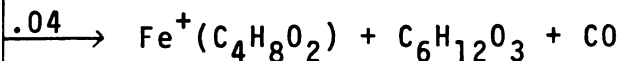
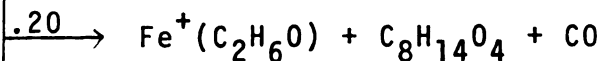
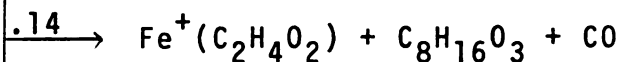
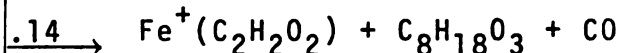
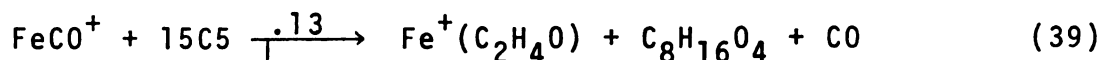
Most products of FeCO^+ reactions with 1,3-dioxolan, 1,3-dioxane and p-dioxane are seen in the Fe^+ case with concurrent loss of CO except as shown in the following:

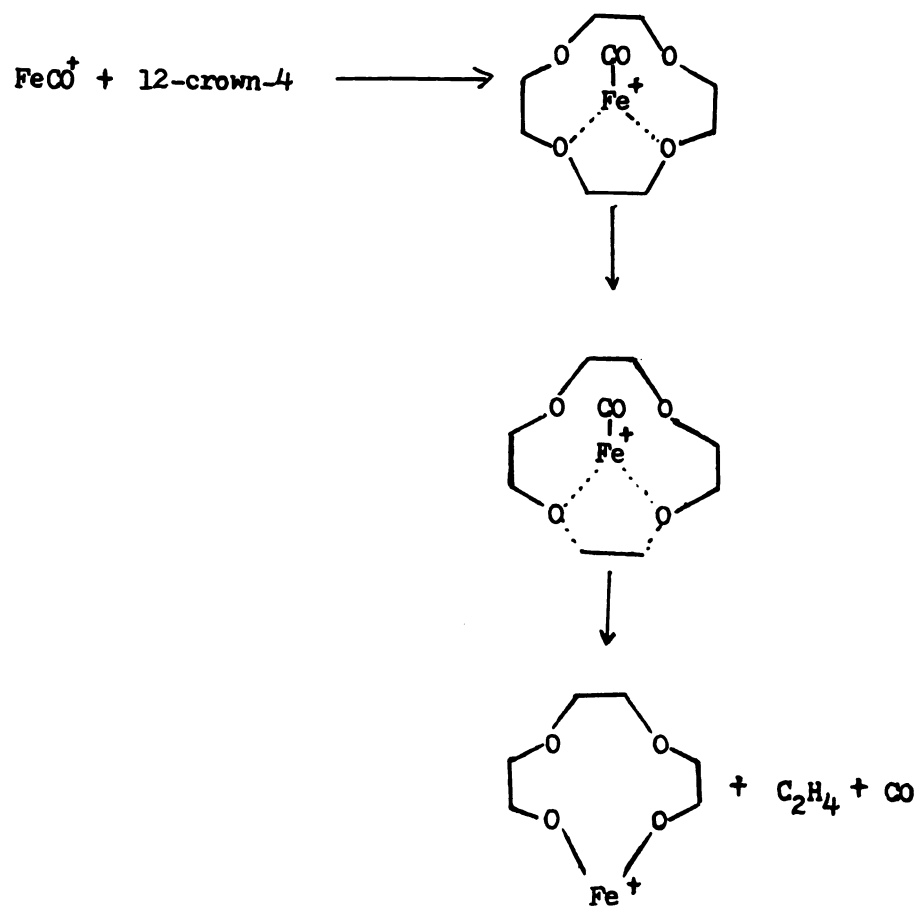
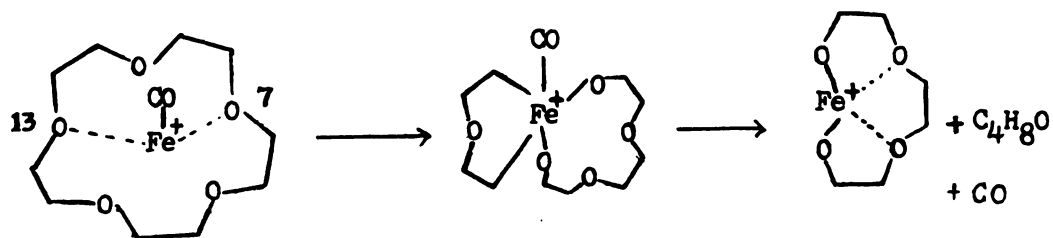


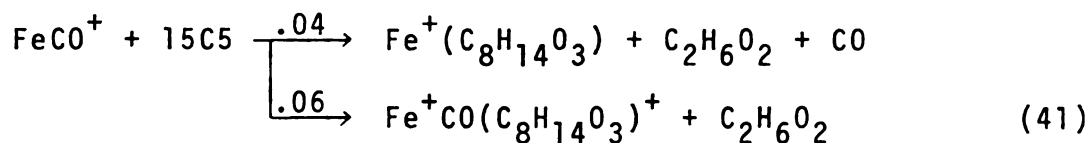
Reactions (30), (34) and (36) are typical of ligand substitution processes. In the 1,3-dioxolane, 1,3-dioxane, p-dioxane systems, the addition complexes are reactive enough to undergo successive reactions (31) (32) (35) (37) and (38). Note that the reaction products in (31) and (35) are also formed from $\text{Fe}(\text{CH}_2\text{O})^+$, which is reactive too. Presumably, CH_2O in reaction (33) carries away most of the reaction energy, leaving CO retained by Fe^+ .

FeCO^+ forms seven products with 12-crown-4; six of them were also formed by Fe^+ alone. Thus, MCO^+ insertion does not appear to predominate in the reactions with the cyclic polyether. The new product for FeCO^+ with 12-crown-4 is m/e 204; $\text{FeC}_6\text{H}_{12}\text{O}_4^+$, corresponding to loss of CO from the ionic reactant and C_2H_4 from the crown, presumably by a mechanism shown on Scheme XIX.

On the other hand, FeCO^+ forms nine products with 15-crown-5, which are shown below.

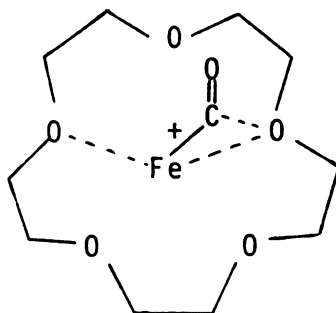


Scheme XIXScheme XX



Of which, six products were also formed by Fe^+ alone. Again, MCO^+ insertion does not seem to play a role in this larger cyclic polyether.

The new product $\text{Fe}(\text{C}_2\text{H}_4\text{O})^+$ in reaction (39) is presumably formed via the mechanism shown in Scheme XV, following double insertion as indicated by the pathway b. The CO ligand plays an important role here. Apparently, available energy can be used to break a M^+-CO bond instead of inducing β -H shifts. The product ion $\text{Fe}(\text{C}_6\text{H}_{12}\text{O}_4)^+$ in reaction (40) is formed through interaction with oxygen atoms #7 and #13 as shown in Scheme XX. Note that we do not see this ion in the reaction with Fe^+ . Since oxygen atoms #7 and #13 are far apart, the CO ligand here may play an important role in bringing them closer as shown below:

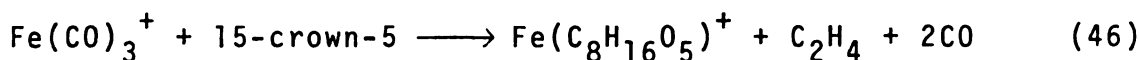
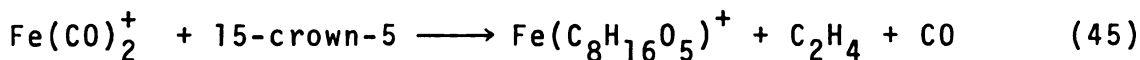
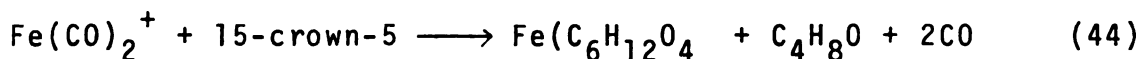
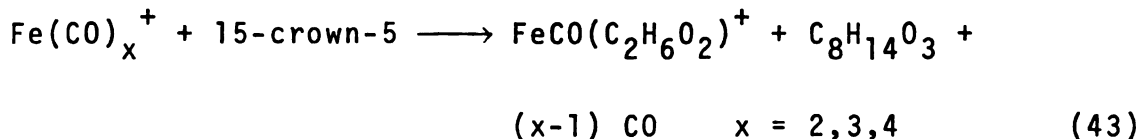
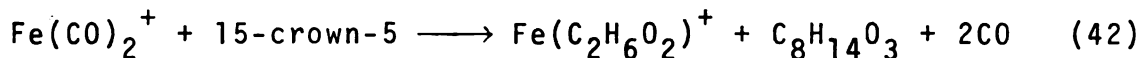


Once Fe^+ double inserts into C-O bonds, it may further interact with oxygen atoms #1 and 4 to eliminate CO and $\text{C}_4\text{H}_8\text{O}$. The retention of CO on the product ion in reaction (41) clearly indicates that no further stabilization energy is produced (product distribution ratio for this ion is 0.06 and only 0.05 in the reaction with Fe^+).

c. $\text{Fe}(\text{CO})_x^+$ reactions with 1,3-dioxolan,
1,3-dioxane, p-dioxane, 12-crown-4 and
15-crown-5.

Higher CO-containing iron ion molecule reactions with 1,3-dioxolan, 1,3-dioxane, p-dioxane and 12-crown-4 only undergo substitutions and successive reactions. Note that in the reactions with 12-crown-4, a new ion, $\text{FeCOC}_2\text{H}_2\text{O}_2^+$ is formed at m/e 142, presumably by the same mechanism as is shown in Scheme XIII.

In the reactions of $\text{Fe}(\text{CO})_x^+$ with 15-crown-5, there are few new ions formed:



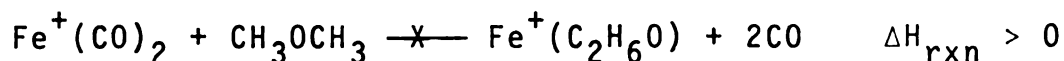
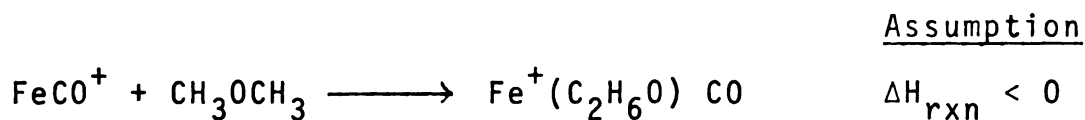
The product ion, $\text{Fe}(\text{C}_6\text{H}_{12}\text{O}_4)^+$ in reaction (44) can be formed by the mechanism shown in Scheme XIX. The loss of 2 CO's might be the result of strong interactions of Fe^+ with oxygen atoms in 15-crown-5. $\text{Fe}(\text{C}_2\text{H}_6\text{O}_2)^+$ and $\text{FeCO}(\text{C}_2\text{H}_6\text{O}_2)^+$ in reactions (42) and (43) are formed by the mechanism shown in Scheme XV. Instead of forming the $\text{Fe}(\text{C}_8\text{H}_{14}\text{O}_3)^+$, which is formed in the Fe^+ and FeCO^+ reactions, these two products are formed by retaining the smaller ligand ($\text{C}_2\text{H}_6\text{O}_2$) with a concurrent loss of 1, 2 or 3 CO's indicating the preference of iron ion to retain the smaller ligands (as noted by the product distribution ratio, .2 for the reaction (42) and only .06 and .05 for the formation of $\text{Fe}(\text{C}_8\text{H}_{14}\text{O}_3)^+$ and $\text{FeCO}(\text{C}_8\text{H}_{14}\text{O}_3)^+$ respectively). Finally, a similar mechanism to that shown in Scheme XIX can be used to explain the formation of $\text{Fe}(\text{C}_8\text{H}_{16}\text{O}_5)^+$ in reactions (45) and (46). Note that as in the 12-crown-4 case, CO ligands appear to be important in forming this big metallocyclic product, since the energy which can be used for β -H shifts is instead used to break $\text{M}^+\text{-CO}$ bonds.

4. Thermodynamic Conclusions

Table 6 lists all neutrals lost in the $\text{Fe}(\text{CO})_x^+$ reactions with linear ethers, polyether, cyclic ethers and polyethers which we have just discussed in last sections and branching ratios. (Product distributions)

Fe^+ induces the rearrangement of dimethylether into CH_2O and CH_4 , but FeCO^+ does not. This can be readily

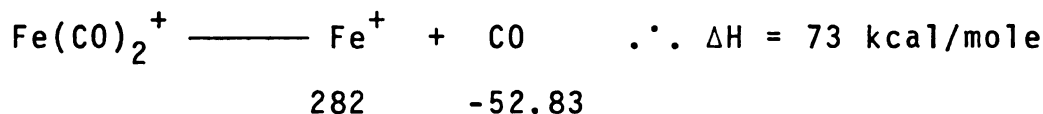
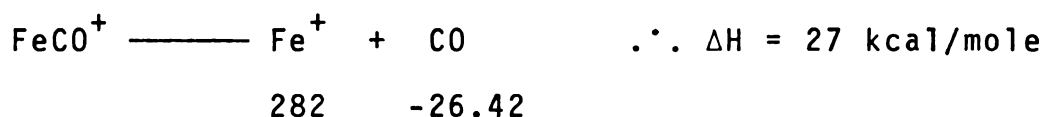
understood in terms of thermodynamics: (Dimethylether will displace one, but not two CO's from Fe^+)



This implies that the initial Fe^+ -dimethylether interaction energy is $27.17 \text{ kcal/mole} < D(\text{Fe}^+ - \text{Me}_2\text{O}) < 73.17 \text{ kcal/mole}$.

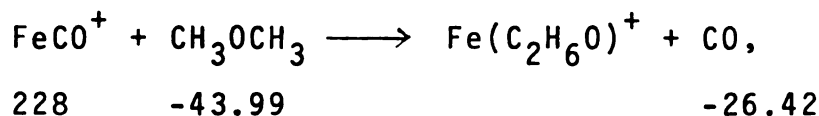
Note that there are two ways to interpret these results. (All ΔH_f 's are taken from ref. 142 and all units are in kcal/mole).

A. In terms of bondstrengths

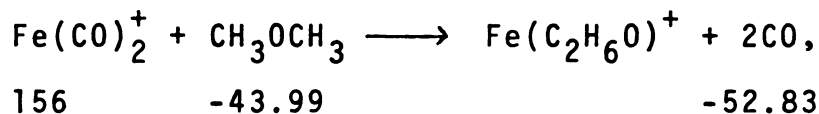


$$\therefore 27 \text{ kcal/mole} < D(\text{Fe}^+ - \text{Me}_2\text{O}) < 73 \text{ kcal/mole}$$

B. In terms of heats of formation

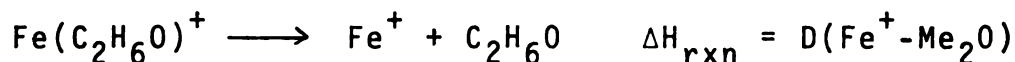


$$\therefore \Delta H_f(\text{Fe}^+-\text{Me}_2\text{O}) < 210$$



$$\therefore \Delta H_f(\text{Fe}^+-\text{Me}_2\text{O}) > 165$$

But,



$$\therefore D(\text{Fe}^+-\text{Me}_2\text{O}) = \Delta H_f(\text{Fe}^+) + \Delta H_f(\text{Me}_2\text{O}) -$$

$$\Delta H_f(\text{Fe}^+-\text{Me}_2\text{O}) = 282 + (-43.99) -$$

$$[165 < \Delta H_f(\text{Fe}^+\text{Me}_2\text{O}) < 210]$$

$$\therefore 28 \text{ kcal/mole} < D(\text{Fe}^+-\text{Me}_2\text{O}) < 73 \text{ kcal/mole}$$

If, however, the structure of $\text{Fe}(\text{C}_2\text{H}_6\text{O})^+$ is really $\text{CH}_3\text{-Fe}^+-\text{OCH}_3$, then

$$D(\text{CH}_3\text{-Fe}^+-\text{OCH}_3) = \Delta H_f(\text{Fe}^+) + \Delta H_f(\text{CH}_3) + \Delta H_f(\text{OCH}_3) -$$

$$\Delta H_f(\text{CH}_3\text{-Fe}^+-\text{OCH}_3) = 282 + 34.3 + 3.5 - \left(\begin{array}{l} > 165 \\ < 210 \end{array} \right)$$

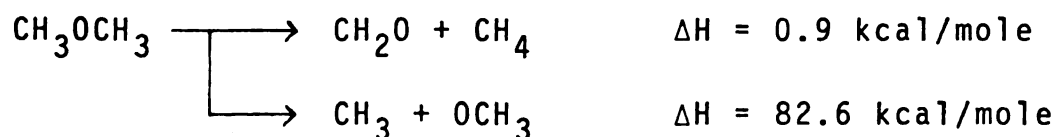
$$\therefore 109 \text{ kcal/mole} < D(\text{CH}_3\text{-Fe}^+-\text{OCH}_3) < 155 \text{ kcal/mole}$$

Table 1.1. Reactions and ΔH° with known

Reagent							1,3-diene-5				TS	1,2-cyclo-6
H^+	C_6H_8 (77) Ac (77)	C_5H_6 (13) C_5H_6 (13) Ac (13)	C_4H_4 (13) C_4H_4 (13) Ac (13)	C_3H_2 (13) C_3H_2 (13) Ac (13)	C_3H_4 (13) C_3H_4 (13) Ac (13)	C_4H_6 (13) C_4H_6 (13) Ac (13)	C_5H_6 (13) C_5H_6 (13) Ac (13)	C_5H_6 (13) C_5H_6 (13) Ac (13)	C_6H_8 (13) C_6H_8 (13) Ac (13)	C_6H_8 (13) C_6H_8 (13) Ac (13)	TS	1,2-cyclo-6
H_2O^+	C_6H_8 (13) C_6H_8 (13) Ac (13)	C_5H_6 (13) C_5H_6 (13) Ac (13)	C_4H_4 (13) C_4H_4 (13) Ac (13)	C_3H_2 (13) C_3H_2 (13) Ac (13)	C_3H_4 (13) C_3H_4 (13) Ac (13)	C_4H_6 (13) C_4H_6 (13) Ac (13)	C_5H_6 (13) C_5H_6 (13) Ac (13)	C_5H_6 (13) C_5H_6 (13) Ac (13)	C_6H_8 (13) C_6H_8 (13) Ac (13)	C_6H_8 (13) C_6H_8 (13) Ac (13)	TS	1,2-cyclo-6
H_2O^+	C_6H_8 (13) C_6H_8 (13) Ac (13)	C_5H_6 (13) C_5H_6 (13) Ac (13)	C_4H_4 (13) C_4H_4 (13) Ac (13)	C_3H_2 (13) C_3H_2 (13) Ac (13)	C_3H_4 (13) C_3H_4 (13) Ac (13)	C_4H_6 (13) C_4H_6 (13) Ac (13)	C_5H_6 (13) C_5H_6 (13) Ac (13)	C_5H_6 (13) C_5H_6 (13) Ac (13)	C_6H_8 (13) C_6H_8 (13) Ac (13)	C_6H_8 (13) C_6H_8 (13) Ac (13)	TS	1,2-cyclo-6
H_2O^+	C_6H_8 (13) C_6H_8 (13) Ac (13)	C_5H_6 (13) C_5H_6 (13) Ac (13)	C_4H_4 (13) C_4H_4 (13) Ac (13)	C_3H_2 (13) C_3H_2 (13) Ac (13)	C_3H_4 (13) C_3H_4 (13) Ac (13)	C_4H_6 (13) C_4H_6 (13) Ac (13)	C_5H_6 (13) C_5H_6 (13) Ac (13)	C_5H_6 (13) C_5H_6 (13) Ac (13)	C_6H_8 (13) C_6H_8 (13) Ac (13)	C_6H_8 (13) C_6H_8 (13) Ac (13)	TS	1,2-cyclo-6

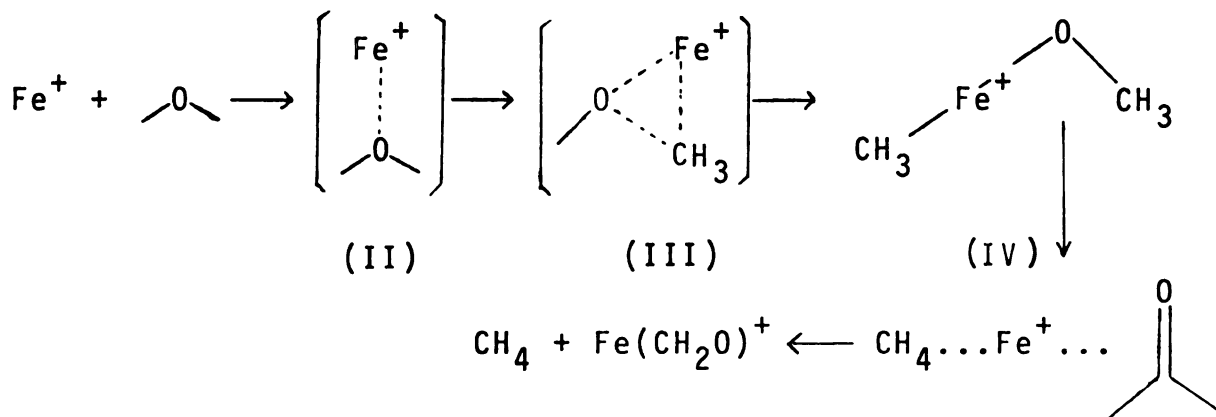
* 1,2 more addition complex

Also, the energies required to rearrange/fragment the organic molecule are 0.9 kcal/mole and 82.6 kcal/mole for the following two processes respectively



Obviously, the first process (involves Fe^+ insertion into C-O bond, followed by a β -shift) is a low energy process, which has to pass through an intermediate (insertion product) related to second process, in which the insertion product is formed. Although β -H shifts might not require energy (i.e. naturally occur), the extra energy after forming the insertion product will be removed by the $\text{Fe}^+\text{-CO}$ bond breaking ($\approx 27.8 \text{ kcal/mole}$)¹⁴² to get no further reaction and stop at $\text{Fe}(\text{CH}_2\text{O})^+$.

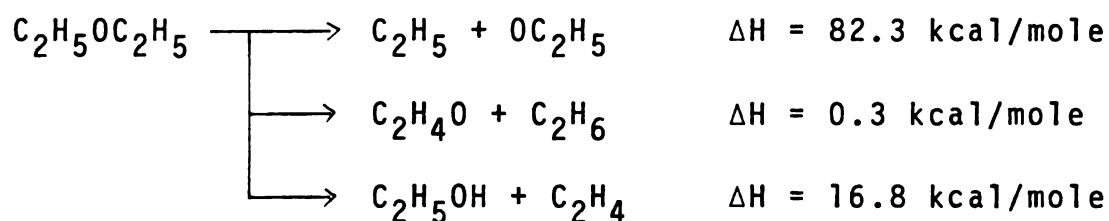
Since the initial complexation energy is smaller than the energy required to dissociate dimethylether into CH_3 and OCH_3 , the real mechanism might look like:



Fe^+ reacts with dimethylether to form (IV) with much energy released which is available for further reactions. However this energy will be taken away by a CO ligand in the FeCO^+ reaction. This explains why precursors of (IV) are composed of only 8.6% of Fe^+ and 91.4% of FeCO^+ (see Appendix F).

Analogously, diemthylether will displace up to three CO's from Fe^+ implying that the initial Fe^+ -diethylether interaction energy is $96.6 \text{ kcal/mole} < D(\text{Fe}^+-\text{Et}_2\text{O}) < 133.3 \text{ kcal/mole}$.

The energies required for Fe^+ insertion into a C-O bond in diethylether, and for rearrangement procuts are:



The second process is the lowest energy process among these three processes. A possible reason why the formation of $\text{Fe}(\text{C}_2\text{H}_5\text{OH})^+$ can displace up two CO's from Fe^+ and only one CO for forming $\text{Fe}(\text{C}_2\text{H}_4\text{O})^+$ is that Fe^+ may form a stronger bond with $\text{C}_2\text{H}_5\text{OH}$ than that of $\text{C}_2\text{H}_4\text{O}$. However, it is not understandable what makes so much difference in complexation energy of Fe^+ with dimethylether from that of diethylether. Could it be from the polarizability difference?

The rest of the reactions can be explained in a similar way. The data to date can be summarized as follows:

1. Whenever β -H atoms are available, they will shift to form stable products, following insertion into a C-O bond. If CO ligands are present, the breaking of M^+-CO bonds may compete with this process.

2. A stable addition complex can only be formed with the concurrent loss of one or more CO ligand on the metal ion (to take away the energy).

3. A "mechanistic macrocyclic effect"¹⁴³ is seen. In the case of 12-crown-4, the Fe^+ actually induces reactions to product 9 products, but only one product is observed in its linear analog (TDE).

4. In the case of 12-crown-4, we assume that the Fe^+ actually induces reactions from "inside" the crown cavity. This is implied by the fact that Fe^+ reacts with 12-crown-4 to form 9 different products, $FeCO^+$ gives 7 products, $Fe(CO)_2^+$ gives only 2 products, and as more CO's are added to the metal, no reactions are observed. Thus, ligands can prevent the metal from entering the crown cavity and inducing reactions¹⁴³. However, this may not be true in the 15-crown-5 case, which has a larger crown cavity. Hence, Fe^+ reacts with 15-crown-5 to form 7 products, $FeCO^+$ gives 9 products, $Fe(CO)_2^+$ gives 6 products and both $Fe(CO)_3^+$ and $Fe(CO)_4^+$ give 2 products respectively.

5. Many products of reactions involving cyclic polyethers, 12-crown-4 and 15-crown-5 can be explained using a double metal insertion, double β -H shifts process. In these

reactions, CO ligands act predominately as spectators.

6. When CO's are present on the metal center, they can act either as spectator ligands or as active groups (vis MCO^+ insertion). An alternate interpretation is that, after M^+-C bonds are formed, a CO ligand on the metal may insert into the M^+-C bond.

7. The strength of a metal-ligand bond alone does not guarantee complexation in the species studied here. In the case of bulky ligands, the presence of 3CO's on a metal center may prohibit sufficiently close approach for insertion.

II. $\text{Cr}(\text{CO})_x^+$ Reactions With Ethers And Polyethers

A. Results

1. Linear Ethers and Polyethers

a. $\text{Cr}^+(\text{CO})_x$ reaction with dimethylether($\text{C}_2\text{H}_6\text{O}$)

Ions formed as products of ion-molecule reactions in a mixture of $\text{Cr}(\text{CO})_6$ and dimethylether are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
98	$\text{Cr}(\text{C}_2\text{H}_6\text{O})^+$	Cr^+CO , $\text{Cr}(\text{CO})_2^+$
126	$\text{CrCO}(\text{C}_2\text{H}_6\text{O})^+$	$\text{Cr}(\text{CO})_2^+$, $\text{Cr}(\text{CO})_3^+$
144	$\text{Cr}(\text{C}_2\text{H}_6\text{O})_2^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$, $\text{Cr}(\text{CO})_3^+$, $\text{Cr}(\text{CO})_4^+$

b. Cr(CO)_x^+ reaction with diethylether
 $(\text{C}_4\text{H}_{10}\text{O})$

Ions formed as products of ion-molecule reactions in a mixture of Cr(CO)_6 and diethylether are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
96	$\text{Cr(C}_2\text{H}_4\text{O)}^+$	Cr^+
110	$\text{Cr(C}_3\text{H}_6\text{O)}^+$	CrCO^+
126	$\text{Cr(C}_4\text{H}_{10}\text{O)}^+$	Cr^+ , CrCO^+ , Cr(CO)_2^+
149	$(\text{C}_4\text{H}_{10}\text{O})_2\text{H}^+$	OCH_3^+ , OC_2H_5^+ , $\text{C}_4\text{H}_{11}\text{O}^+$

The ion at m/e 149 is $(\text{C}_4\text{H}_{10}\text{O})_2\text{H}^+$, the protonated diethylether's dimer is formed by $\text{C}_4\text{H}_{11}\text{O}^+$ reaction with a neutral molecule of diethylether, which in turn is formed by OCH_3^+ and OC_2H_5^+ .

c. Cr(CO)_x^+ reaction with triethylene glycol
dimethylether (TDE, $\text{C}_8\text{H}_{18}\text{O}_4$)

Ions formed as products of ion-molecule reactions in a mixture of Cr(CO)_6 and TDE are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
84	$\text{Cr(CH}_4\text{O)}^+$	CrCO^+ , Cr(CO)_2^+
91	$\text{C}_4\text{H}_{11}\text{O}_2^+$	$\text{C}_2\text{H}_3\text{O}^+$
96	$\text{Cr(C}_2\text{H}_4\text{O)}^+$	Cr^+
98	$\text{Cr(C}_2\text{H}_6\text{O)}^+$	CrCO^+ , Cr(CO)_2^+ , Cr(CO)_3^+
101	$\text{C}_5\text{H}_9\text{O}_2^+$	$\text{C}_3\text{H}_6\text{O}^+$ or $\text{C}_2\text{H}_2\text{O}_2^+$

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
110	$\text{Cr}(\text{C}_3\text{H}_6\text{O})^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$
112	$\text{CrCO}(\text{CH}_4\text{O})^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$
126	$\text{Cr}(\text{C}_3\text{H}_6\text{O}_2)^+$	Cr^+ , CrCO^+ , $\text{Cr}(\text{CO})_2^+$
128	$\text{Cr}(\text{C}_3\text{H}_8\text{O}_2)^+$	Cr^+ , CrCO^+ , $\text{Cr}(\text{CO})_2^+$
138	$\text{CrCOC}_3\text{H}_6\text{O}^+$	$\text{Cr}(\text{CO})_2^+$
140	$\text{Cr}(\text{CO})_2\text{CH}_4\text{O}^+$	$\text{Cr}(\text{CO})_2^+$, $\text{Cr}(\text{CO})_3^+$
142	$\text{Cr}(\text{C}_4\text{H}_{10}\text{O}_2)^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$
156	$\text{CrCOC}_3\text{H}_8\text{O}_2^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$
166	$\text{Cr}(\text{CO})_2\text{C}_3\text{H}_6\text{O}^+$	$\text{Cr}(\text{CO})_2^+$
168	$\text{CrCOC}_4\text{H}_8\text{O}_2^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$, $\text{CrCOC}_3\text{H}_6\text{O}^+$
170	$\text{CrCOC}_4\text{H}_{10}\text{O}_2^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$, $\text{CrCOC}_3\text{H}_6\text{O}^+$

2. Cyclic Ethers and Polyethers

a. $\text{Cr}(\text{CO})_x^+$ reactions with tetrahydrofuran (THF, $\text{C}_4\text{H}_8\text{O}$)

Ions formed as products of ion-molecule reactions in a mixture of $\text{Cr}(\text{CO})_6$ and THF are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
124	$\text{Cr}(\text{C}_4\text{H}_8\text{O})^+$	Cr^+ , CrCO^+ , $\text{Cr}(\text{CO})_2^+$
152	$\text{CrCO}(\text{C}_4\text{H}_8\text{O})^+$	$\text{Cr}(\text{CO})_2^+$, $\text{Cr}(\text{CO})_3^+$, $\text{Cr}(\text{CO})_4^+$
196	$\text{Cr}(\text{C}_4\text{H}_8\text{O})_2^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$, $\text{Cr}(\text{CO})_3^+$, $\text{Cr}(\text{CO})_4^+$, $\text{Cr}(\text{C}_4\text{H}_8\text{O})^+$, $\text{CrCO}(\text{C}_4\text{H}_8\text{O})^+$

b. Cr(CO)_x^+ reactions with tetrahydropyran
(THF, $\text{C}_5\text{H}_{10}\text{O}$)

Ions formed as products of ion-molecule reactions in mixture of Cr(CO)_6 and THP are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
110	$\text{Cr(C}_3\text{H}_6\text{O)}^+$	Cr^+ , CrCO^+
138	$\text{Cr(C}_5\text{H}_{10}\text{O)}^+$	Cr^+ , CrCO^+ , Cr(CO)_2^+
166	$\text{CrCO(C}_5\text{H}_{10}\text{O)}^+$	Cr(CO)_2^+ , Cr(CO)_3^+
224	$\text{Cr(C}_5\text{H}_{10}\text{O)}_2^+$	Cr^+ , CrCO^+ , Cr(CO)_2^+ , $\text{Cr(C}_5\text{H}_{10}\text{O)}^+$

c. Cr(CO)_x^+ reactions with 1,3 dioxolan
($\text{C}_3\text{H}_6\text{O}_2$)

Ions formed as products of ion-molecule reactions in a mixture of Cr(CO)_6 and 1,3-dioxolan are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
82	$\text{Cr(CH}_2\text{O)}^+$	Cr^+
126	$\text{Cr(C}_3\text{H}_6\text{O}_2)^+$	Cr^+ , CrCO^+ , Cr(CO)_2^+
154	$\text{CrCO(C}_3\text{H}_6\text{O}_2)^+$	Cr(CO)_2^+ , Cr(CO)_3^+
156	$\text{Cr(C}_3\text{H}_6\text{O}_2)(\text{CH}_2\text{O)}^+$	Cr^+ , CrCO^+ , Cr(CO)_2^+ , $\text{Cr(C}_3\text{H}_6\text{O}_2)^+$

d. Cr(CO)_x^+ reactions with 1,3-dioxane
 $(\text{C}_4\text{H}_8\text{O}_2)$

Ions formed as products of ion-molecule reactions in a mixture of Cr(CO)_6 and 1,3-dioxane are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
82	$\text{Cr(CH}_2\text{O)}^+$	Cr^+
110	$\text{Cr(C}_3\text{H}_6\text{O)}^+$	Cr^+
112	$\text{Cr(C}_2\text{H}_4\text{O}_2)^+$	Cr^+
140	$\text{Cr(C}_4\text{H}_8\text{O}_2)^-$	Cr^+ , CrCO^+ , Cr(CO)_2^+
144	$\text{C}_7\text{H}_{12}\text{O}_3^+$	C_3H_5^+ , $\text{C}_2\text{H}_5\text{O}^+$, $\text{C}_4\text{H}_7\text{O}_2^+$
168	$\text{CrCO(C}_4\text{H}_8\text{O}_2)^+$	Cr(CO)_2^+ , Cr(CO)_3^+
170	$\text{Cr(C}_4\text{H}_8\text{O}_2)(\text{CH}_2\text{O})^+$ or $\text{Cr(C}_2\text{H}_4\text{O}_2)(\text{C}_3\text{H}_6\text{O})^+$	Cr^+ , CrCO^+ , $\text{Cr(C}_2\text{H}_4\text{O}_2)^+$
196	$\text{Cr(CO)}_2(\text{C}_4\text{H}_8\text{O}_2)$	Cr(CO)_4^+
197	$\text{Cr(CO)}_2\text{C}_4\text{H}_9\text{O}_2^+$	$\text{C}_3\text{H}_7\text{O}^+$ or $\text{C}_2\text{H}_3\text{O}_2^+$
228	$\text{Cr(C}_4\text{H}_8\text{O}_2)_2^+$	Cr^+ , CrCO^+ , Cr(CO)_2^+ , $\text{Cr(C}_4\text{H}_8\text{O}_2)^+$, Cr(CO)_3^+ , $\text{CrCO(C}_4\text{H}_8\text{O}_2)^+$, Cr(CO)_4^+

e. Cr(CO)_x^+ reactions with p-dioxane $(\text{C}_4\text{H}_8\text{O}_2)$
and its d_8 isotope

Ions formed as products of ion-molecule reactions in a mixture of Cr(CO)_6 and 1,4-dioxane and p-dioxane- d_8 are listed in Table 7, with their precursors as identified by double resonance.

Table 7. $\text{Cr}(\text{CO})_6$ Reaction With P-dioxane And P-dioxane- d_8 -

p-dioxane			p-dioxane- d_8		
m/e	stoichiometry	precursor(s)	m/e	stoichiometry	precursor(s)
82	$\text{Cr}(\text{CH}_2\text{O})^+$	Cr^+	84	$\text{Cr}(\text{CD}_2\text{O})^+$	Cr^+
140	$\text{Cr}(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Cr}^+, \text{CrCO}^+$	148	$\text{Cr}(\text{C}_4\text{D}_8\text{O}_2)^+$	$\text{Cr}^+, \text{CrCO}^+$
168	$\text{CrCO}(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Cr}(\text{CO})_2^+$	176	$\text{CrCO}(\text{C}_4\text{D}_8\text{O}_2)^+$	$\text{Cr}(\text{CO})_2^+$
228	$\text{Cr}(\text{C}_4\text{H}_8\text{O}_2)_2^+$	$\text{Cr}(\text{CO})_2^+, \text{Cr}(\text{CO})_3^+$ $\text{CrCO}^+, \text{Cr}(\text{CO})_2^+$	194	$\text{CD}_2\text{OCr}(\text{CO})_4^+$	CD_2O^+
		$\text{Cr}(\text{C}_4\text{H}_8\text{O}_2)^+, \text{CrCO}(\text{C}_4\text{H}_8\text{O}_2)^+$	244	$\text{Cr}(\text{C}_4\text{D}_8\text{O}_2)_2^+$	$\text{Cr}^+, \text{Cr}(\text{CO})_2^+$ $\text{Cr}(\text{C}_4\text{D}_8\text{O}_2)^+$

f. Cr(CO)_x^+ reactions with 12-crown-4
 $(\text{C}_8\text{H}_{16}\text{O}_4)$

Ions formed as products of ion-molecule reactions in a mixture of Cr(CO)_6 and 12-crown-4 are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
96	$\text{CrC}_2\text{H}_4\text{O}^+$	Cr^+
112	$\text{CrC}_2\text{H}_4\text{O}_2^+$	Cr^+
128	$\text{CrC}_2\text{H}_4\text{O}_3^+$	Cr^+
156	$\text{CrC}_4\text{H}_8\text{O}_3^+$	Cr^+ , CrCO^+ , Cr(CO)_2^+
200	$\text{CrC}_6\text{H}_{12}\text{O}_4^+$	Cr^+ , CrCO^+ , Cr(CO)_2^+
228	$\text{CrC}_8\text{H}_{16}\text{O}_4^+$	Cr^+ , CrCO^+ , Cr(CO)_2^+

g. Cr(CO)_x^+ reactions with 15-crown-5
 $(\text{C}_{10}\text{H}_{20}\text{O}_5)$

Ions formed as products of ion-molecule reactions in a mixture of Cr(CO)_6 and 15-crown-5 are listed below, with their precursors as identified by double resonance.

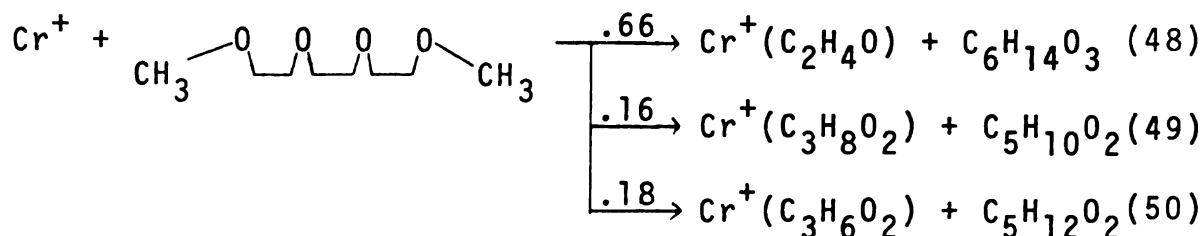
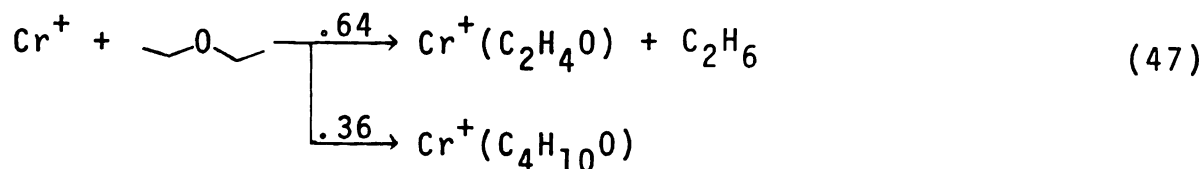
<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
110	$\text{Cr(C}_2\text{H}_2\text{O}_2)^+$	CrCO^+
113	$\text{Cr(C}_2\text{H}_5\text{O}_2)^+$	CrCO^+ , Cr(CO)_2^+
126	$\text{Cr(C}_4\text{H}_{10}\text{O})^+$	Cr^+
156	$\text{Cr(C}_4\text{H}_8\text{O}_3)^+$	Cr^+ , CrCO^+
200	$\text{Cr(C}_6\text{H}_{12}\text{O}_4)^+$	Cr^+ , CrCO^+ , Cr(CO)_2^+

B. Discussion

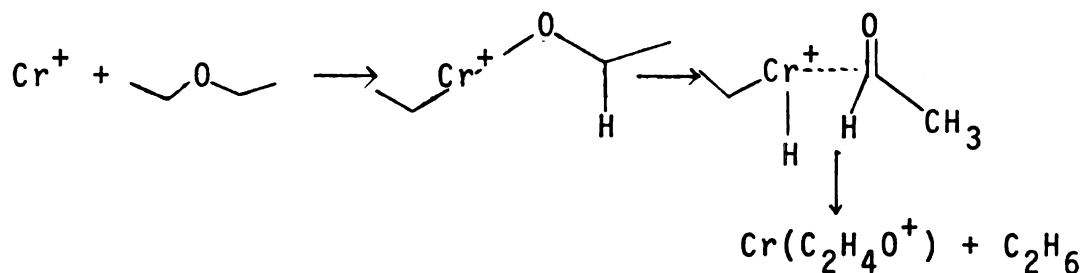
1. Linear Ethers and Polyether

a. Reactions of Cr^+

Cr^+ does not react with dimethylether. Products of Cr^+ reactions with diethylether and TDE are listed in the following.



Reactions (47)-(50) can be explained again based on what was discussed in the case of Fe^+ , namely, metal ion insertion, followed by a β -hydrogen shift. This is shown below and in Scheme XXI.



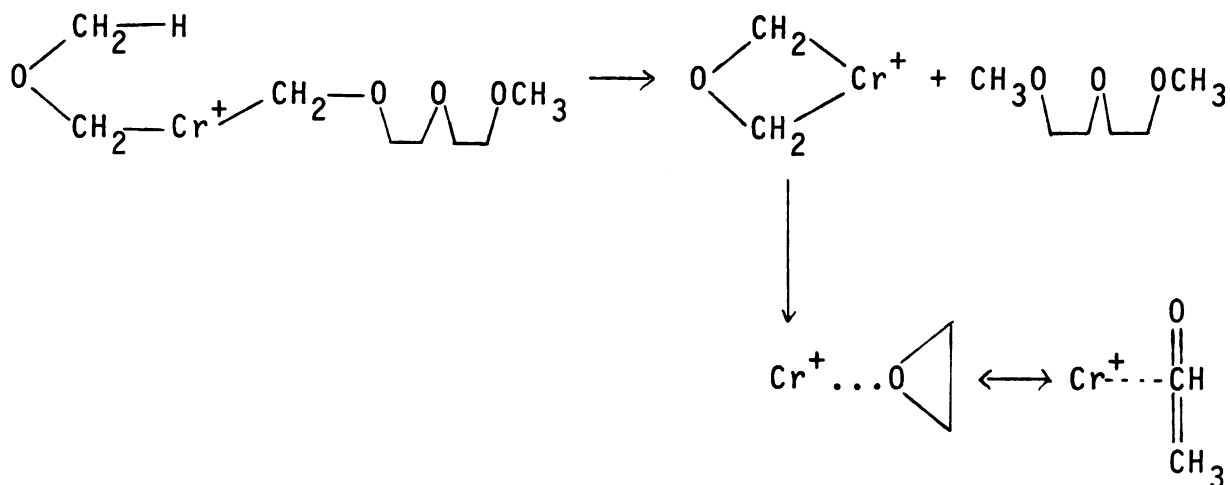
Note that $\text{Cr}^+(\text{C}_3\text{H}_8\text{O}_2)$ and $\text{Cr}^+(\text{C}_3\text{H}_6\text{O}_2)$ in reactions (49) (50) are formed following insertion into the bond between skeletal atoms 5 and 6, which is in contrast to Fe^+

which inserts into the bond between skeletal atoms 4 and 5 (p. 56). Attack of a more centrally located bond in the polyether may be evidence for a symmetric intermediate involving multiple metal-ligand interactions. This possibility is shown as the first step in Scheme XXI.

Also, the strong $\text{Cr}^+ \text{-O}$ interaction ($D(\text{Cr}^+ \text{-O}) = 77 \pm 5$ kcal/mole) may favor the formation of small ligands with more oxygen's than does Fe^+ - explaining the difference in site of attack for Fe^+ and Cr^+ . In Scheme VXi, both possible β -H atoms can shift to get corresponding products. However, there is only one β -H shift which occurs in the case of Fe^+ . The probability of such a H-shift depends on the stability of the final product. Both pathways in Scheme XXI form ligands which can donate 4 electrons to the electron deficient metal. Thus, the option of which β -H's will shift is related in part to the ability of the final product to be a good ligand (strong bond to Fe^+).

Cr^+ also reacts with TDE to form $\text{CrC}_2\text{H}_4\text{O}^+$ (reaction (48)). A variety of mechanisms have been considered, however none are consistent with other mechanisms and observations. We can speculate that, to form a rearrangement product consisting of 2 carbons and one oxygen, an insertion into the bond between skeletal atoms 3 and 4 by Cr^+ would be necessary. However, this intermediate, has no H atoms which are β - to the metal. The intermediate, written as follows, shows that a six-membered ring intermediate could

form a 4-membered ring product $\text{CrC}_2\text{H}_4\text{O}^+$ with subsequent loss of $\text{CH}_3(\text{OC}_2\text{H}_4)_2\text{OCH}_3$.

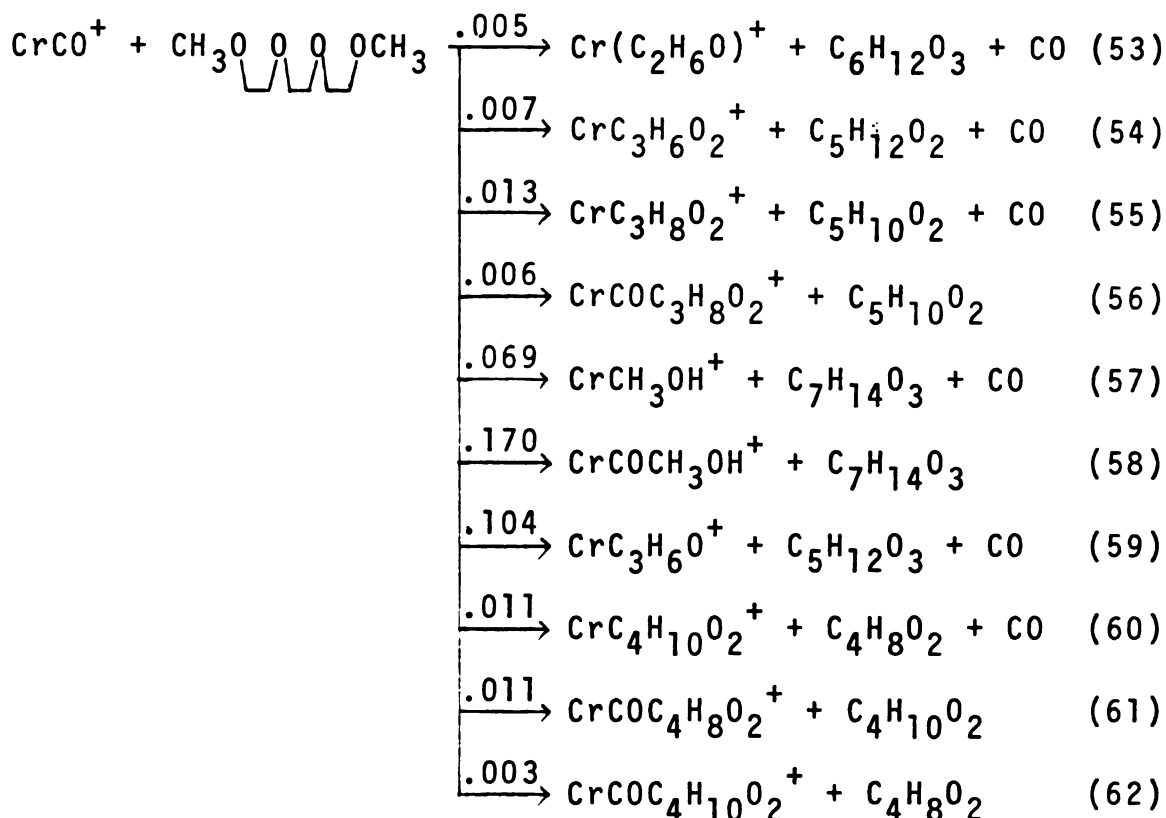
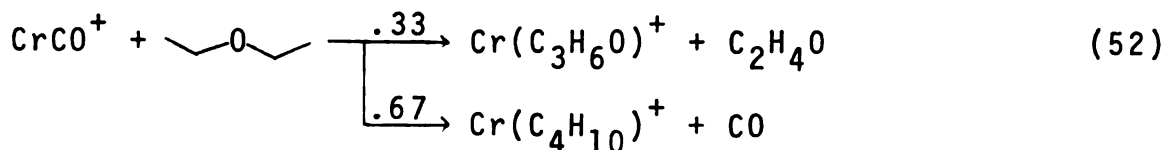
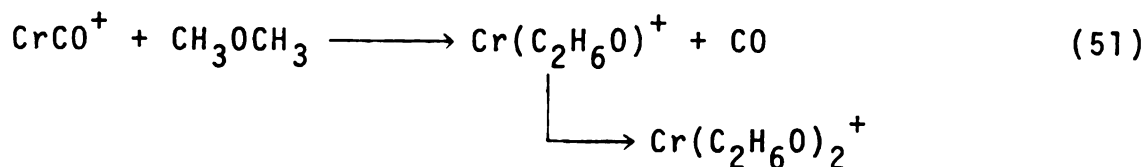


Note that the explanation above is based on Cr^+ insertion into a C-C bond instead of a C-O bond, which is not usual, because Cr^+ -alkyl bonds are weak.

TDE, then, appears to react via the same mechanism as diethylether. Cr^+ and Fe^+ apparently choose to attack different C-O bonds of this polyether. This choice may be in part forced by the structure of the initial metal-ligand complex, and further favored by the stabilities of the final products.

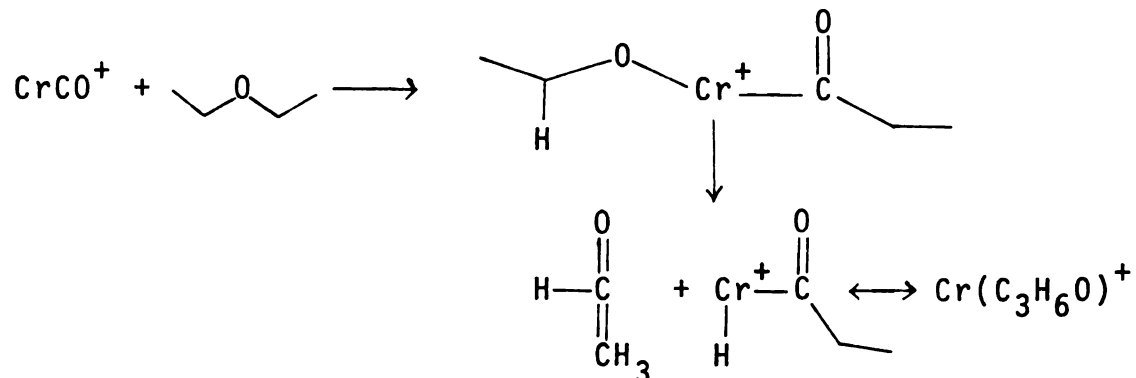
b. Reactions of CrCO^+

The CrCO^+ reactions with dimethylether, diethylether and TDE are summarized on the next page:



CrCO^+ reactions with dimethylether and diethylether only result in ligand substitution and successive reactions. The product in (52) is not formed by Cr^+ alone. If the metal inserted into a C-C bond, there would be no β -H shift and eliminate CH_4 . Thus, we conclude that the CO of CrCO^+ is actively involved in the process and inserts in toto into

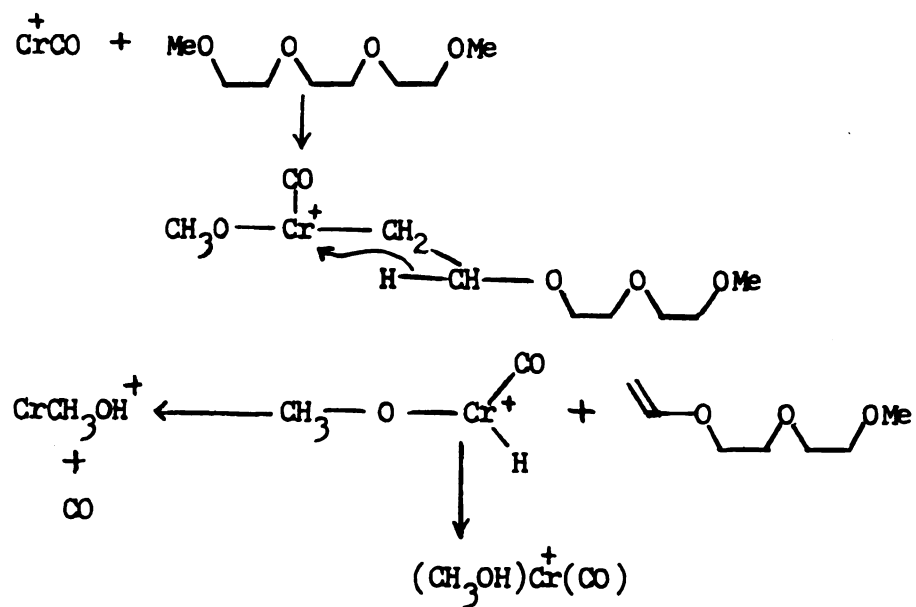
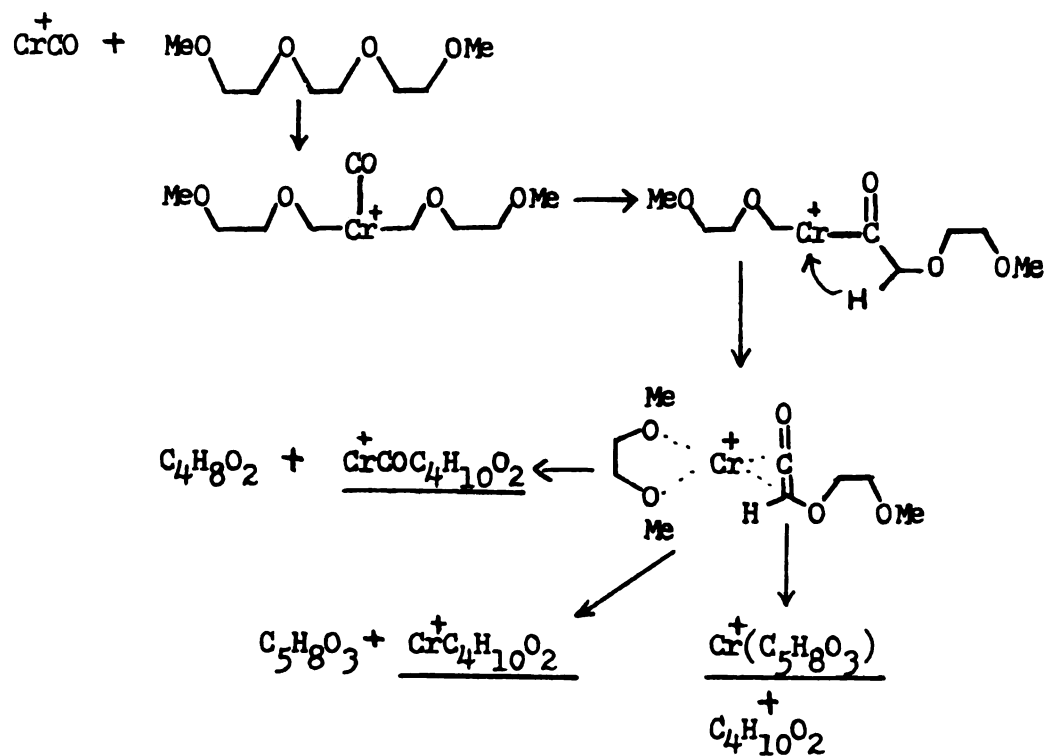
the C-O ether bond. Based on past observations, the neutral product of (52) could be C_2H_4O or $[CO \text{ and } CH_4]$.



This mechanism leads to acetaldehyde as the neutral lost in (52).

The products in (54)-(56) were formed by Cr^+ alone, and thus have been discussed in Scheme XXI. Apparently $CrCO^+$ extracts methanol from TDE. Cr^+ alone does not do so, however the CO is not actively involved in the mechanism, since both $CrCH_3OH^+$ and $CrCOCH_3OH^+$ are products. Thus, we interpret this via M^+ insertion process, in which the CO acts as a spectator ligand as shown in Scheme XXII. Once the metal center has induced the elimination of methanol from TDE the $Cr(CH_3OH)(CO)^+$ can use the remaining available energy to break the weaker metal ligand bond, Cr^+-CO .

The products in (60)-(62) can also be explained by $CrCO^+$ insertion into the central skeletal bond of TDE as shown in Scheme XXIII. Note that both $CrCOC_4H_8O_2^+$ and $CrCOC_4H_{10}O_2^+$ have a small contribution from m/e 138, $CrCOC_3H_6O^+$, as their precursor, however, it would not be

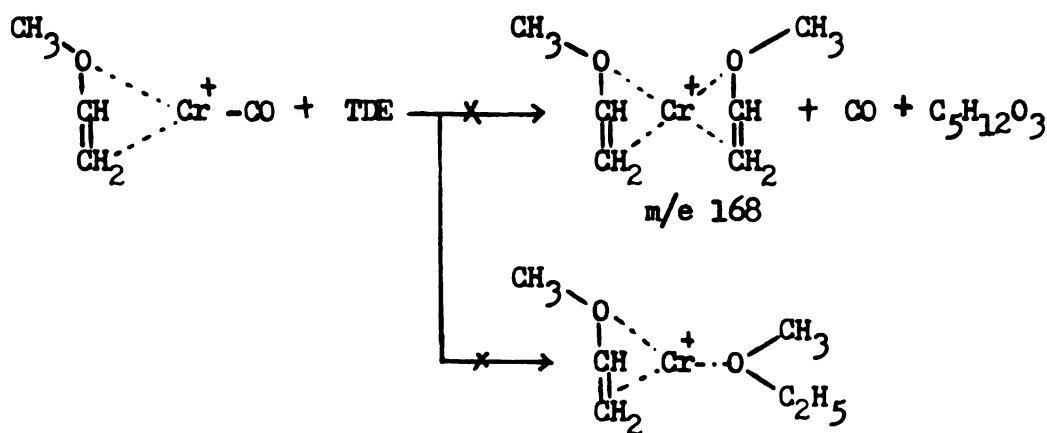
Scheme XXII.Scheme XXIII

expected to be reactive enough to experience successive reactions with large molecule like TDE.*

Also note that the formation of $\text{CrCOC}_4\text{H}_{10}\text{O}_2^+$ illustrated in Scheme XXIII occurs when CrCO^+ inserts into a C-C bond, followed by a β -H shift, and the CO is retained on the metal center.

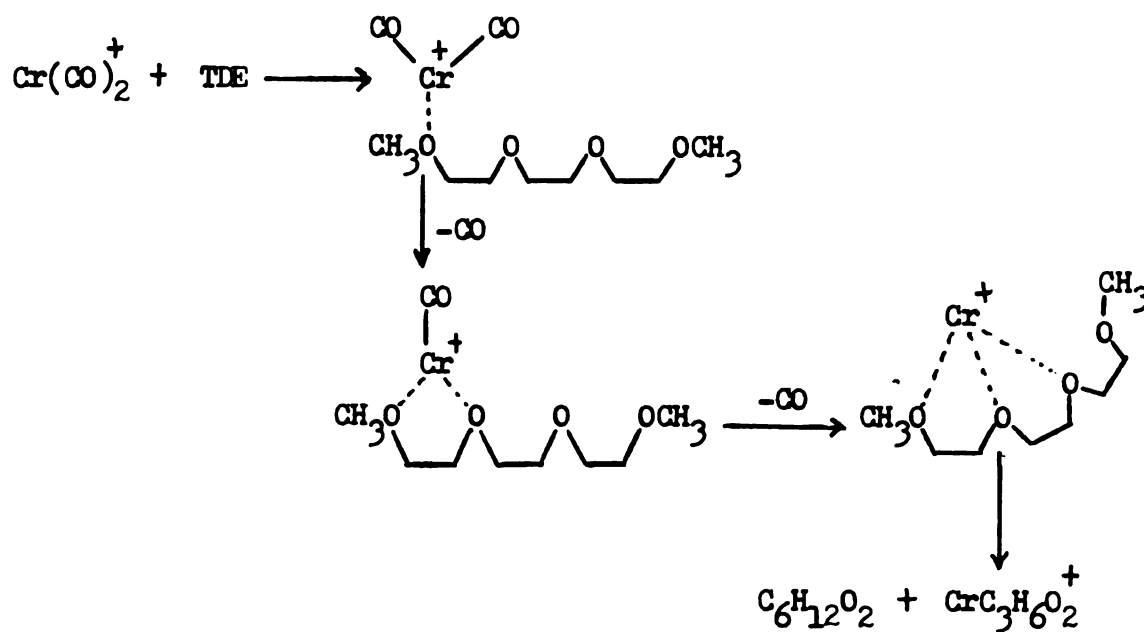
Products in (59) are formed by the same mechanism as in Fe^+ case, where the metal ion inserts into a C-O bond (skeletal atoms 4 and 5), followed by a β -H shift. Since Cr^+ does not do so, but both $\text{CrC}_3\text{H}_6\text{O}_2^+$ and $\text{CrCOC}_3\text{H}_6\text{O}_2^+$ are products, the CO on Cr^+ might be a spectator as described above in the formation of CrCH_3OH^+ . The formation of $\text{Cr}(\text{C}_2\text{H}_6\text{O})^+$ in reaction (53) is again explained by CrCO^+ insertion into skeletal atoms 3 and 4, so that β -H is available for shifting.

* This is based on the assumption that a large molecule such as TDE has a steric effect which could prevent $\text{CrCOC}_3\text{H}_6\text{O}^+$ from approaching TDE to do any insertion, β -H shift process i.e.



c. Reactions of $\text{Cr}(\text{CO})_x^+$

Higher CO-containing chromium ion reactions with diemthylether, and diethylether only give substitution reactions. However, it is more striking to realize that all of the products for TDE are reactive rearrangement of TDE - none are simple CO displacements. This may reflect the ability of TDE to complex stepwise with the metal center i.e. - initial complexation may involve one oxygen of the ligands. As further oxygens interact, additional energy is made available for metal-induced decomposition of the polyether e.g.

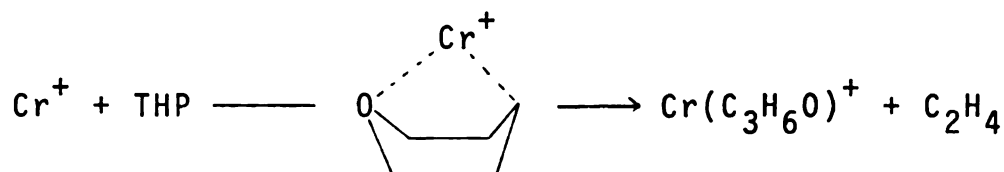


CO here also acts as an energy mediator to stabilize the system, so that Cr^+ can interact with another oxygen without decomposing.

2. Cyclic Ethers

a. Reactions of Cr^+

Cr^+ doesn't react with THF except by forming an addition complex. It reacts with THP to form only one product, $\text{Cr}(\text{C}_3\text{H}_6\text{O})^+$, which can be explained analogously to Fe^+



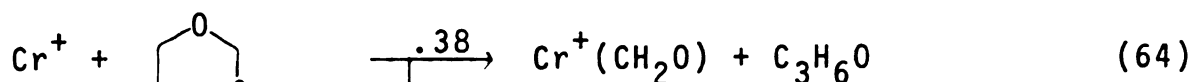
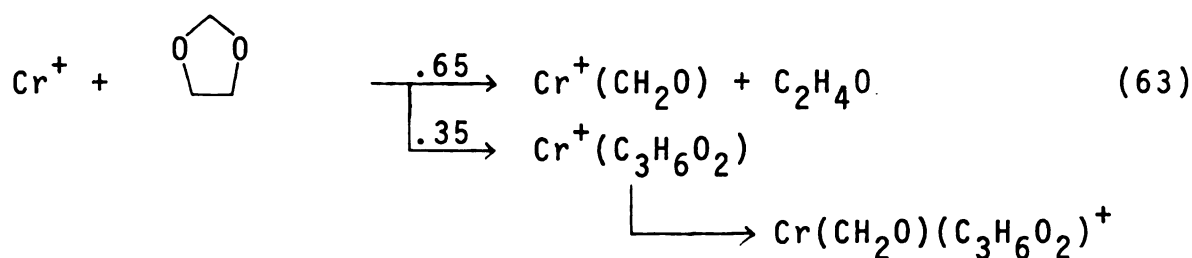
3. Cyclic Polyethers

a. Reactions of Cr^+

Cr^+ reactions with 1,3-dioxolan, 1,3-dioxane, p-dioxane (d_8), 12-crown-4 and 15-crown-5 are summarized in Table 8.

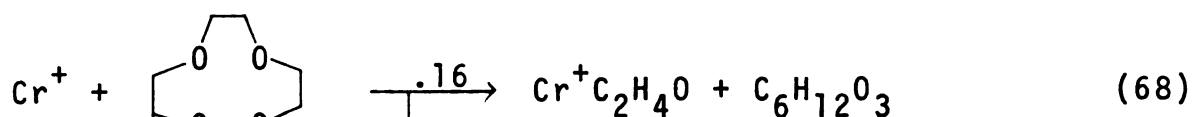
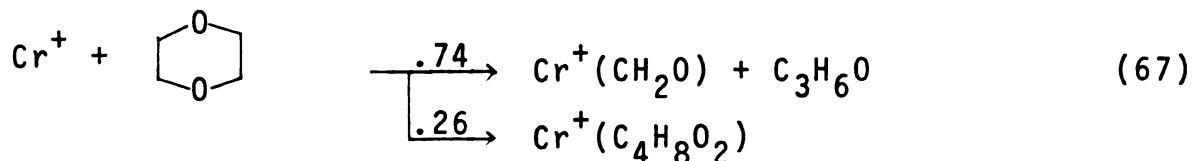
Presumably, the products in (63), (64), (65), (66), (67) can be explained in terms of the mechanisms which have been proposed for Fe^+ (p. 64) for the reaction of Cr^+ with 1,3-dioxolan, 1,3-dioxane and p-dioxane. Note that Cr^+ is even more "selective" compared with Fe^+ . Cr^+ reactions with 1,3-dioxolan and 1,4-dioxane give only one product, $\text{Cr}(\text{CH}_2\text{O})^+$. On the hand, the reaction of Cr^+ with 1,3-dioxane produces the same products as Fe^+ except for $\text{Cr}(\text{C}_2\text{H}_4)^+$. Two important factors may control these product distributions:

(1) Cr^+ forms strong bonds with oxygen (77 ± 5 kcal/mole,

Table 8. Cr⁺ Reactions With Cyclic Polyethers

(65)

(66)

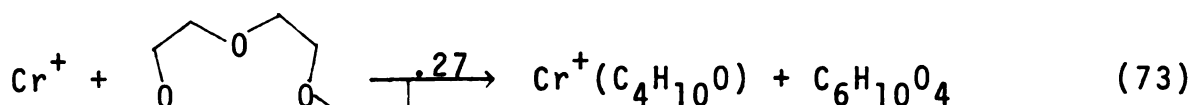


(69)

(70)

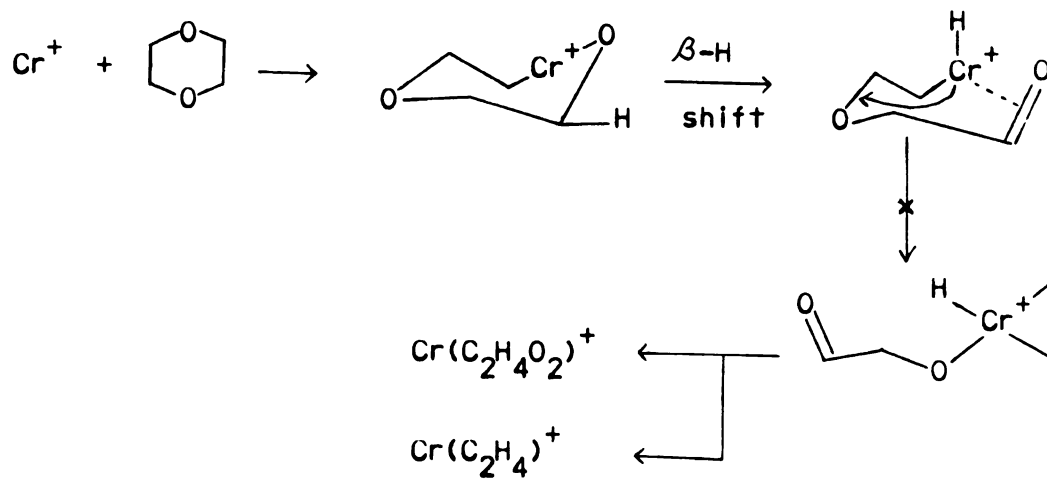
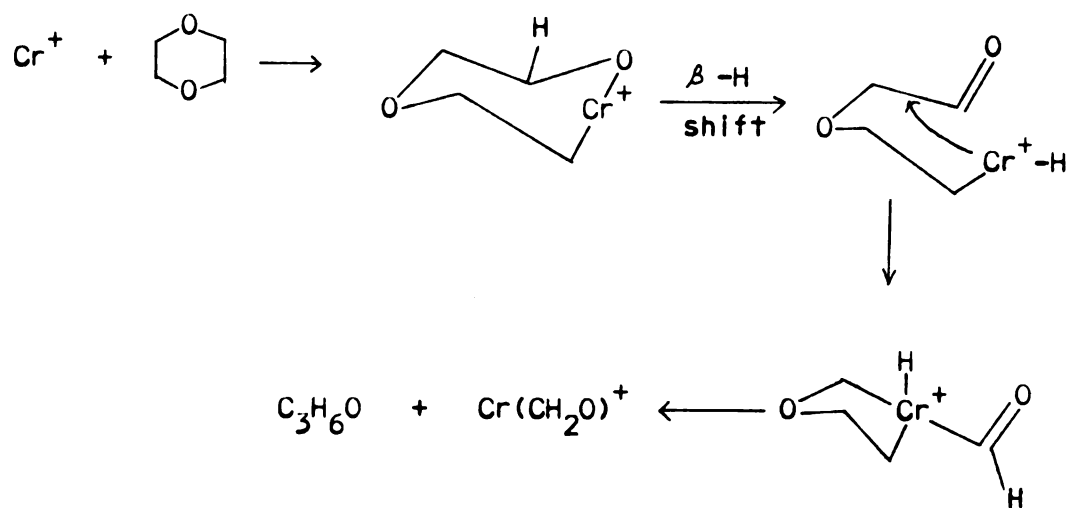
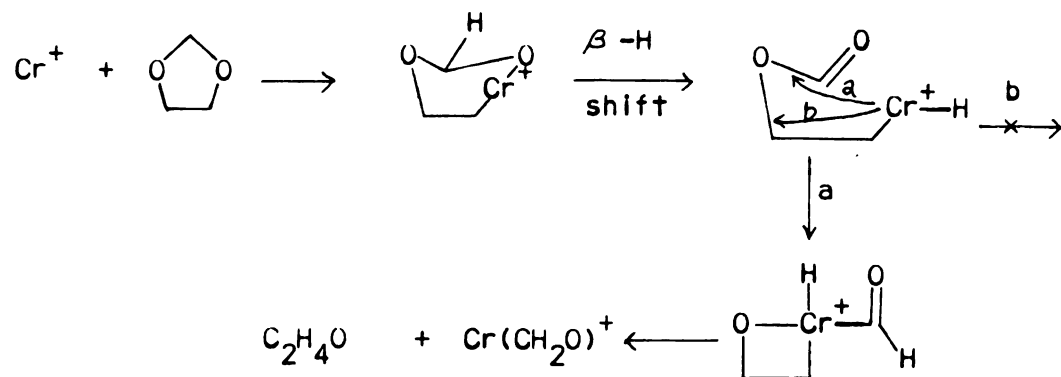
(71)

(72)



(74)

(75)

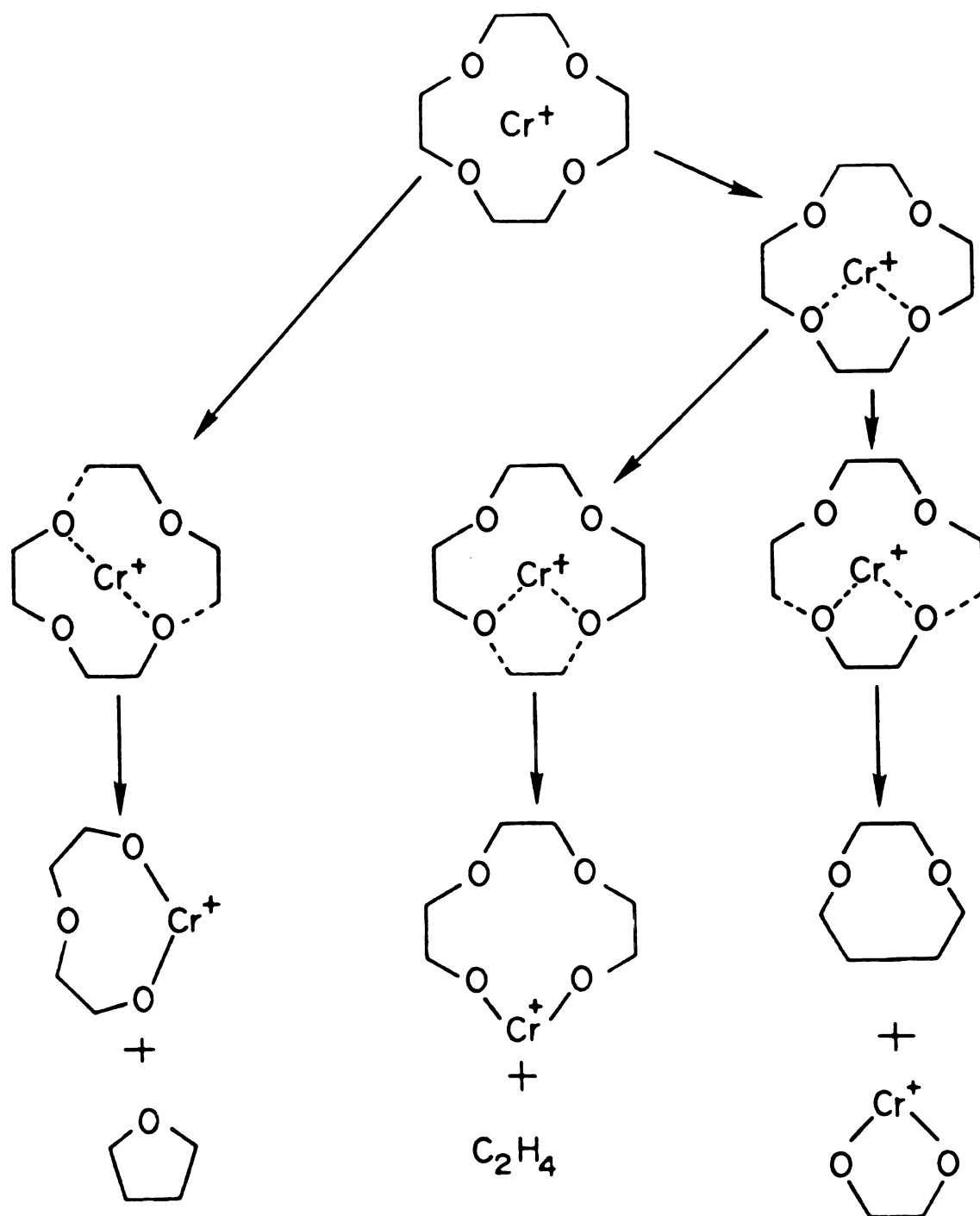


see (Table 2) compared with $\text{Cr}^+-\text{C}(\text{H}_2)(\text{R})$ (37 ± 7 kcal/mole), that is, it may prefer to produce products having a high O/C ratio and bonds to oxygen atom directly. (2) Stepwise metal ion double insertion, followed by β -H's shift is occurring so that chromium can insert into a bond which is in geometrical proximity, due to a weaker initial complexation energy as a driving force (see thermodynamic conclusion section) as shown on page 113.

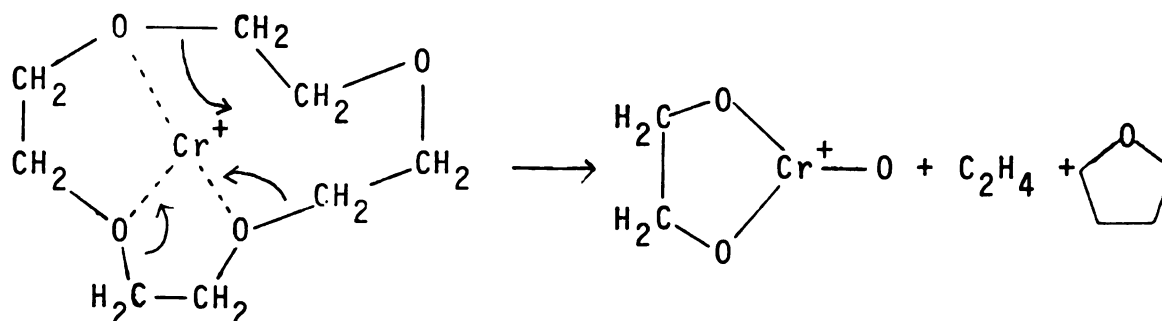
The chemistry of Cr^+ with 12-crown-4 differs from that of Fe^+ , apparently due to the fact that, relative to Fe^+ , Cr^+ interacts more strongly with oxygen and less strongly with carbon.

The first product, $\text{CrC}_2\text{H}_4\text{O}^+$ in (68) could be explained using a mechanism similar to that in Scheme XII. Note that products in (69)-(72) have ligands with a higher O:C ratio than those formed in Table 5 with Fe^+ . Consider the product $\text{CrC}_2\text{H}_4\text{O}_2^+$. This could be considered as either Cr^+ complexed to $\text{OC}_2\text{H}_4\text{O}$ or as a metallocyclic 5-membered ring. The latter will be assumed because of the strong Cr^+-O bond. These products can then be explained if the Cr^+ complexes in the crown cavity, and, because of its size, can only interact with two oxygens at a time. Apparently no H-shifts occur. The pathways leading to products (69), (71), (72) are shown in Scheme XXIV. Note that all pairwise combinations of oxygens are sampled.

The product in (70) has a very high O:C ratio in the

SCHEME ~~XXIV~~

ionic product, and may be the result of the metal ion "puckering" up the molecule in an attempt to interact with 3 oxygens of the crown.



It is striking to notice that Cr^+ forms an adduct ion (addition complex) with 12-crown-4. Again, this could be the result of the small metal ion puckering up the molecule in an attempt to interact with 3 or 4 oxygens of the crown as some alkali metal ions do¹¹⁷. However it is hard to interact all 4 oxygens because Cr^+ has a larger size than the cavity of 12-crown-4, (Cr^+ has a radius of $0.81 \text{ \AA}$ ^{146,147}, compared with the cavity of 12-crown-4 which is $1.2 \text{ \AA}$ - $1.5 \text{ \AA}$ in diameter), Cr^+ must be to some extent "away" from the cavity center, which would result in a longer range interactions (ionic rather than covalent)* with all four oxygens and no bond breaking will occur. Fe^+ has the same tendency for interacting with both oxygen atoms and carbon.

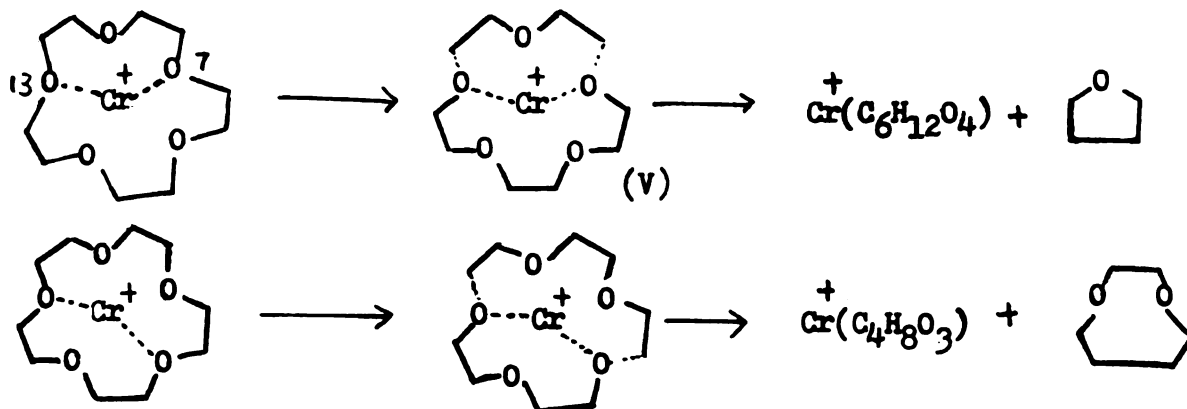
* Cr^+ has a $6s$ ground state corresponding to an $[\text{Ar}] 3d^5$ configuration¹⁵⁷. The next excited state is $6d$ at 1.47 V , corresponding to $[\text{Ar}] 4s 3d^4$. Despite the energy gap of 1.47 eV , it was reported that a long-lived metastable excited state of Cr^+ exists in ICR on electron impact on $\text{Cr}(\text{CO})_6$ ^{141,148}. It is not surprising that $\text{Cr}^+(6s)$ will interact with oxygen atoms electrostatically through both intrinsic and induced dipoles. To form covalent bonds, it has to use an sd hybrid and $\text{Cr}(6d)$ will form covalent bonds with oxygens.

If they interact, energy is released and much chemistry occurs, since it can only form bonds covalently. Thus Cr^+ exhibits quite a different chemistry with 12-crown-4 than does Fe^+ . This can be accounted for by the greater preference of Cr^+ for bonding to oxygen, which appears to be the predominant driving force in the Cr^+ reactions.

The attempt to interact with 3 and 4 oxygens by Cr^+ is also observed in its reaction with 15-crown-5. Products in reactions (74) and (75), namely $\text{Cr}(\text{C}_4\text{H}_8\text{O}_3)^+$ and $\text{Cr}(\text{C}_6\text{H}_{12}\text{O}_4)^+$ were formed by the mechanism shown in Scheme XXV, in which Cr^+ need only make an effort to pucker oxygen atom #1, since oxygen atoms #7, 4, 13 are already on the same plane.

The product in (73) can be explained by a mechanism similar to that of in Scheme XIV - after forming an intermediate (V) in Scheme XXV, Cr^+ inserts into two C-O bonds, followed by double β -H shifts to form $\text{Cr}(\text{C}_4\text{H}_{10}\text{O})^+$.

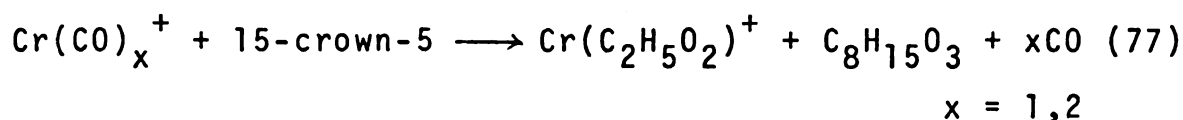
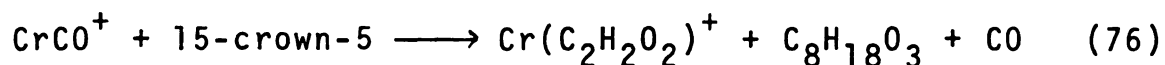
Scheme XXV.



b. Reactions of Cr(CO)_x^+

Cr(CO)_x^+ ($x = 1-6$) reactions with 1,3-dioxolan, 1,3-dioxane, p-dioxane, 12-crown-4 only result in the addition complexes, substitution reactions and successive reactions.

Cr(CO)_x^+ reactions with 15-crown-5 yield two new products:



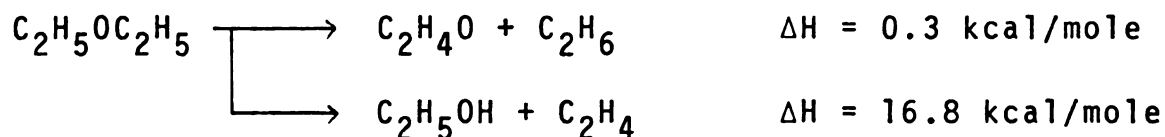
Products in (76) and (77) can be explained by a mechanism similar to that shown in Scheme XIII. Formation of $\text{Cr(C}_2\text{H}_5\text{O}_2\text{)}^+$ may be an indication that Cr^+ is sequentially inserting into C-O bonds, followed by β -H shifts to avoid an intermediate with an unusually high formal oxidation state for the metal. Further β -H shifts might not occur if they are geometrically inaccessible after one β -H shifts. Referring to Scheme XIII, no products corresponding to double or single β -H shifts from the larger ring side are observed. Since Cr^+ has a strong bond energy with oxygen atoms, the formation of products in reactions (76) and (77) is accompanied by the loss of CO to carry away the extra energy.

4. Thermodynamic Conclusions

Table 9 lists all neutral lost in the $\text{Cr}(\text{CO})_x^+$ reactions with all the ethers discussed above and their branching ratios (product distributions).

Dimethylether can displace up to two CO's from Cr^+ , as can diethylether, implying that the initial Cr^+ -ether interaction, $66.2 \text{ kcal/mole} < D(\text{Cr}^+-\text{Me}_2\text{O}), D(\text{Cr}^+-\text{Et}_2\text{O}) < 87.7 \text{ kcal/mole}$, is less than that of Fe^+ , $96.6 \text{ kcal/mole} < D(\text{Fe}^+-\text{Et}_2\text{O}) < 133.3 \text{ kcal/mole}$, but larger than that of the dimethylether case, $27.17 \text{ kcal/mole} < D(\text{Fe}^+-\text{Me}_2\text{O}) < 73.17 \text{ kcal/mole}$.

Cr^+ can only react with diethylether by H-shift pathway (p. , Scheme X) to get $\text{Cr}(\text{C}_2\text{H}_4\text{O})^+$. The difference from that of Fe^+ may be in part thermodynamics. Recall,



Cr^+ can induce the rearrangement indicated in the first process, which requires very little energy, $\Delta H = 0.3 \text{ kcal/mole}$. Fe^+ induces both rearrangements. More energy is required for the second process, $\Delta H = 16.8 \text{ kcal/mole}$. Thus Fe^+ forms "higher energy" products than does Cr^+

However, one must be careful when thermodynamic conclusions are drawn for Cr^+ , since electron impact on $\text{Cr}(\text{CO})_6$ produces excited states of $\text{Cr}^{+141,148}$. Nevertheless,

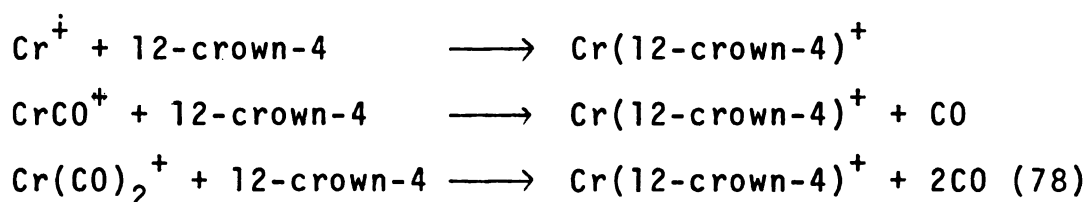
Table 9. Neutrals Lost In The Reactions Of $\text{Cr}(\text{O})_x^+$ With Ethers

									12-crown-4	15-crown-5
Cr^+	C_2H_6 (.64) AC (.36)						C_2H_6 (.74) AC (.26)		$\text{C}_6\text{H}_{10}\text{O}_4$ (.27) $\text{C}_6\text{H}_{12}\text{O}_2$ (.60) $\text{C}_4\text{H}_8\text{O}$ (.04)	
$\text{Cr}(\text{O})^+$	$\text{C}_2\text{H}_6\text{O}$ (.33) ∞ (.67)								$\text{C}_6\text{H}_{10}\text{O}_3$ (.16) $\text{C}_6\text{H}_{12}\text{O}_2$ (.17) $\text{C}_6\text{H}_{10}\text{O}$ (.34) $\text{C}_6\text{H}_{12}\text{O}$ (.25) $\text{C}_4\text{H}_8\text{O}$ (.03) AC (.05)	$\text{C}_8\text{H}_{18}\text{O}_3 + \text{O}$ (.12) $\text{C}_8\text{H}_{15}\text{O}_3 + \text{O}$ (.20) $\text{C}_6\text{H}_{12}\text{O}_2 + \text{O}$ (.42) $\text{C}_4\text{H}_8\text{O} + \text{O}$ (.26)
$\text{Cr}(\text{O})_2^+$	200 ∞	200 ∞	200 ∞	200 100	200 ∞	200 ∞	200 ∞	200 ∞	$\text{C}_4\text{H}_8\text{O} + 2\text{O}$ (.28) $\text{C}_2\text{H}_6 + 2\text{O}$ (.11) 200 (.61)	$\text{C}_8\text{H}_{15}\text{O}_3 + 2\text{O}$ (.31) $\text{C}_4\text{H}_8\text{O} + 2\text{O}$ (.67)
$\text{Cr}(\text{O})_3^+$	200	200	200	200	200	200	200	200		
$\text{Cr}(\text{O})_4^+$										

* AC means addition complex

although the dissociation energy of dimethylether into CH_2O and CH_4 is only 0.9 kcal/mole, we neither see $\text{Cr}(\text{CH}_2\text{O})^+$, nor addition complex from Cr^+ . The reason for this is not clear.

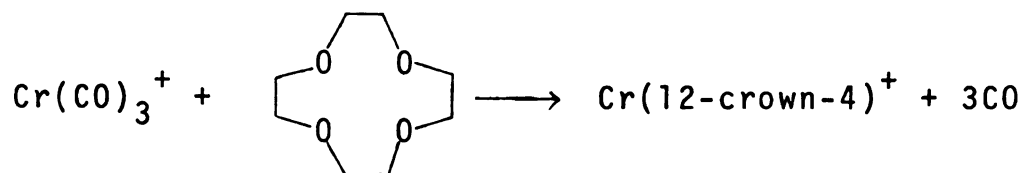
It is of interest to note that no ion of composition $\text{Cr}(\text{TDE})^+$ or $\text{Fe}(\text{TDE})^+$ was observed. In the case of 12-crown-4, no ion of composition $\text{Fe}(\text{12-crown-4})^+$ was observed. $\text{Cr}(\text{12-crown-4})^+$ is formed, with 3 precursors:



Since $\text{Cr}(\text{CO})_3^+$ is not a precursor to $\text{Cr}(\text{12-crown-4})^+$, one may interpret this as an indication of the Cr^+ -crown bond strengths:

$$\begin{aligned}D(\text{Cr}^+-\text{CO}) + D(\text{CrCO}^+-\text{CO}) &< D(\text{Cr}^+-\text{12-crown-4}) < \\ D(\text{Cr}^+-\text{CO}) + D(\text{CrCO}^+-\text{CO}) + D(\text{Cr}(\text{CO})_2^+-\text{CO})\end{aligned}$$

however, this may be an incorrect interpretation. The metal-polyether interactions should be very strong; complexation appears to release enough energy such that subsequent fragmentation of the polyether always occurs, except for Cr^+ , which appears to form weaker bonds to ethers than Fe^+ . Rather, the reaction



may not occur because the carbonyl ligands prevent this large ligand from getting close enough to the metal for significant orbital overlap. This is very graphically seen as we progress from diemthylether to diethylether to TDE to 12-crown-4. The reactions due to M(CO)_n^+ decrease as n increases. Thus, reactions of M^+ alone are presumably due to the metal in or very close to the crown-cavity. As CO's are added to the metal, reactions occur with the metal out of the cavity to the point where CO's prohibit metal-ligand interactions with this bulky ligand. Thus, when 3 or more CO's are present on the metal, sufficiently close approach of the bulky 12-crown-4 ligand is prevented and no reactions, not even simple displacement is observed.

Thus, it is difficult to interpret the data here in terms of estimating M^+ -polyether bondstrengths. The Cr^+ -12-crown-4 bondstrength, based on reaction (78) must be > 66 kcal/mole.

In conclusion, Cr^+ has a weaker complexation energy with ethers than Fe^+ does. Cr^+ doesn't form an adduct ion with 15-crown-5, possibly due to the large cavity of 15-crown-5. As CO's are added to the metal, it only undergoes substitution and successive reactions in smaller ethers.

In the reactions with 12-crown-4 and 15-crown-5, however, the interaction with these bulky ligands is prevented or confined to interact with only a few oxygens in the crowns.

III. Ni(CO)_x^+ Reactions With Ethers and Polyethers

A. Results

1. Linear Ethers and Polyethers

a. Ni(CO)_x^+ reactions with dimethylether (C₂H₆O)

Ions formed as products of ion-molecule reactions in a mixture of Ni(CO)_4 and dimethylether are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
88	$\text{Ni(CH}_2\text{O)}^+$	Ni^+ , NiCO^+
104	$\text{Ni(C}_2\text{H}_6\text{O)}^+$	Ni^+ , NiCO^+
132	$\text{NiCO(C}_2\text{H}_6\text{O)}^+$	Ni(CO)_2^+ , Ni(CO)_3^+
150	$\text{Ni(C}_2\text{H}_6\text{O)}_2^+$	Ni(CO)_2^+ , Ni(CO)_3^+
160	$\text{Ni(CO)}_2\text{(C}_2\text{H}_6\text{O)}^+$	Ni(CO)_3^+ , Ni(CO)_4^+
178	$\text{NiCO(C}_2\text{H}_6\text{O)}_2^+$	Ni(CO)_3^+ , Ni(CO)_4^+
190	$\text{Ni}_2\text{CO(C}_2\text{H}_6\text{O)}^+$	Ni^+ , NiCO^+ , $\text{Ni}_2\text{(CO)}_2^+$
218	$\text{Ni}_2\text{(CO)}_2\text{(C}_2\text{H}_6\text{O)}^+$	Ni^+ , NiCO^+

b. Ni(CO)_x^+ reactions with diethylether (C₄H₁₀O)

Ions formed as products of ion-molecule reactions in a mixture of Ni(CO)_4 and diethylether are listed below, with

their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
86	$\text{Ni}(\text{C}_2\text{H}_4)^+$	Ni^+
102	$\text{Ni}(\text{C}_2\text{H}_4\text{O})^+$	Ni^+ , NiCO^+
104	$\text{Ni}(\text{C}_2\text{H}_5\text{OH})^+$	Ni^+ , NiCO^+
132	$\text{Ni}(\text{C}_4\text{H}_{10}\text{O})^+$	Ni^+ , NiCO^+ , $\text{Ni}(\text{CO})_2^+$
143	$\text{Ni}(\text{CO})_3\text{H}^+$	C_2H_5^+
145	$\text{Ni}(\text{CO})_2(\text{OCH}_3)^+$	CH_3O^+
155	$\text{Ni}(\text{CO})_2\text{C}_3\text{H}_5^+$	C_3H_5^+ , $\text{C}_3\text{H}_7\text{O}^+$
160	$\text{NiCO}(\text{C}_4\text{H}_{10}\text{O})^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
188	$\text{Ni}(\text{CO})_2(\text{C}_4\text{H}_{10})^+$	$\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{CO})_4^+$
191	$(\text{C}_4\text{H}_{10}\text{O})_2(\text{C}_3\text{H}_7)^+$	CH_3O^+
206	$\text{Ni}(\text{C}_4\text{H}_{10}\text{O})_2^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$, $\text{NiCO}(\text{C}_4\text{H}_{10}\text{O})^+$
218	$\text{Ni}_2\text{CO}(\text{C}_4\text{H}_{10}\text{O})^+$	Ni^+ , NiCO^+
234	$\text{NiCO}(\text{C}_4\text{H}_{10}\text{O})_2^+$	$\text{Ni}(\text{CO})_4^+$, $\text{Ni}(\text{CO})_2(\text{C}_4\text{H}_{10}\text{O})^+$

The ion of m/e 143 is a proton transfer product. The ions of m/e 145, 155, 191 are products from organic ion reactions with neutral $\text{Ni}(\text{CO})_4$ formed from OCH_3^+ and C_3H_5^+ .

c. $\text{Ni}(\text{CO})_x^+$ reactions with triethylene glycol dimethylether (TDE, $\text{C}_8\text{H}_{18}\text{O}_4$)

Ions formed as products of ion-molecule reactions in a mixture of $\text{Ni}(\text{CO})_4$ and TDE are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
102	$\text{Ni}(\text{C}_2\text{H}_4\text{O})^+$	Ni^+
103	$\text{NiC}_2\text{H}_5\text{O}^+$	$\text{C}_2\text{H}_3\text{O}^+$, $\text{C}_3\text{H}_7\text{O}^+$
116	$\text{NiC}_3\text{H}_6\text{O}^+$	NiCO^+
118	$\text{Ni}(\text{C}_3\text{H}_8\text{O})^+$	Ni^+ , NiCO^+
130	$\text{NiCO}(\text{C}_2\text{H}_4\text{O})^+$	NiCO^+
133	$\text{Ni}(\text{C}_3\text{H}_7\text{O}_2)^+$	Ni^+ , NiCO^+
134	$\text{Ni}(\text{C}_3\text{H}_8\text{O}_2)^+$	Ni^+ , NiCO^+
144	$\text{NiCO}(\text{C}_3\text{H}_6\text{O})^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
148	$\text{Ni}(\text{C}_4\text{H}_{10}\text{O}_2)^+$	Ni^+ , NiCO^+
160	$\text{NiCO}(\text{C}_3\text{H}_6\text{O}_2)^+$	NiCO^+ , $\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
162	$\text{Ni}(\text{C}_5\text{H}_{12}\text{O}_2)^+$	Ni^+ , NiCO^+ , $\text{Ni}(\text{CO})_2^+$
163	$\text{Ni}(\text{C}_4\text{H}_9\text{O}_3)^+$	Ni^+ , NiCO^+
188	$\text{Ni}(\text{CO})_2(\text{C}_3\text{H}_6\text{O}_2)^+$	$\text{Ni}(\text{C}_2\text{H}_4\text{O})^+$, $\text{Ni}(\text{CO})_3^+$,
	+ $\text{Ni}_2\text{CO}(\text{C}_2\text{H}_4\text{O})^+$	$\text{Ni}(\text{CO})_4^+$
204	$\text{Ni}(\text{C}_7\text{H}_{14}\text{O}_3)^+$	NiCO^+ , $\text{Ni}(\text{CO})_2^+$,
		$\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{CO})_4^+$
221	$\text{Ni}(\text{C}_7\text{H}_{15}\text{O}_4)^+$	NiCO^+ , $\text{Ni}(\text{CO})_2^+$
236	$\text{Ni}(\text{TDE})^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
		$\text{Ni}(\text{CO})_4^+$

2. Cyclic Ethers and Polyethers

a. Ni(CO)_x^+ reactions with tetrahydrofuran (THF, $\text{C}_4\text{H}_8\text{O}$)

Ions formed as products of ion-molecule reactions in a mixture of Ni(CO)_4 and THF are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
100	$\text{Ni(C}_3\text{H}_6)^+$	Ni^+ , NiCO^+
102	$\text{Ni(C}_2\text{H}_4\text{O})^+$	Ni^+ , NiCO^+
112	$\text{Ni(C}_4\text{H}_6)^+$	Ni^+ , NiCO^+
127	$\text{NiCO(C}_3\text{H}_5)^+$	C_3H_5^+
130	Ni(THF)^+	NiCO^+ , Ni(CO)_2^+
155	$\text{Ni(CO)}_2(\text{C}_3\text{H}_5)^+$	C_3H_5^+
158	NiCO(THF)^+	NiCO^+ , Ni(CO)_2^+
186	$\text{Ni(CO)}_2(\text{THF})^+$	Ni(CO)_3^+ , Ni(CO)_4^+
202	Ni(THF)_2^+	NiCO^+ , Ni(CO)_2^+ , Ni(CO)_3^+ , NiCO(THF)^+
216	$\text{Ni}_2\text{CO(THF)}^+$	Ni^+ , NiCO^+ , $\text{Ni}_2(\text{CO})_2^+$
230	$\text{Ni}_2(\text{THF})_2^+$	Ni(CO)_2^+ , Ni(CO)_3^+ , Ni(CO)_4^+ , $\text{Ni(CO)}_2(\text{THF})^+$
244	$\text{Ni}_2(\text{CO})_2(\text{THF})^+$	NiCO

Note that C_3H_5^+ can displace up to 3 CO's from Ni(CO)_4 to produce m/e 127, $\text{NiCO(C}_3\text{H}_5)^+$ and m/e 155, $\text{Ni(CO)}_2(\text{C}_3\text{H}_5)^+$.

b. Ni(CO)_x^+ reactions with tetrahydropyran
 $(\text{THP}, \text{C}_5\text{H}_{10}\text{O})$

Ions formed as products of ion-molecule reactions in a mixture of Ni(CO)_4 and THP are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
112	$\text{Ni(C}_4\text{H}_6)^+$	Ni^+
127	$\text{NiCO(C}_3\text{H}_5)^+$	C_3H_5^+
144	Ni(THP)^+	$\text{NiCO}^+, \text{Ni(CO)}_2^+$
155	$\text{Ni(CO)}_2(\text{C}_3\text{H}_5)^+$	C_3H_5^+
172	NiCO(THP)^+	$\text{Ni(CO)}_2^+, \text{Ni(CO)}_3^+$
206	$\text{Ni(CO)}_2(\text{THP})^+$	$\text{NiCO}^+, \text{Ni(CO)}_3^+, \text{Ni(CO)}_4^+$
230	Ni(THP)_2^+	$\text{NiCO}^+, \text{Ni(CO)}_2^+, \text{Ni(CO)}_3^+$ NiCO(THP)^+

Note that C_3H_5^+ reacts with Ni(CO)_4 to form m/e 127 and m/e 155 as was observed in the mixture containing THF.

c. Ni(CO)_x^+ reactions with 1,3-dioxolan
 $(\text{C}_3\text{H}_6\text{O}_2)$

Ions formed as products of ion-molecule reactions in a mixture of Ni(CO)_4 and 1,3-dioxolan are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
86	$\text{Ni(C}_2\text{H}_4)^+$	Ni^+
88	$\text{Ni(CH}_2\text{O)}^+$	$\text{Ni}^+, \text{NiCO}^+$

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
102	$\text{Ni}(\text{C}_2\text{H}_4\text{O})^+$	Ni^+ , NiCO^+
130	$\text{NiCO}(\text{C}_2\text{H}_4\text{O})^+$	$\text{C}_2\text{H}_4\text{O}^+$
132	$\text{Ni}(\text{C}_3\text{H}_6\text{O}_2)^+$	NiCO^+ , $\text{Ni}(\text{CO})_2^+$
160	$\text{NiCO}(\text{C}_3\text{H}_6\text{O}_2)^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
188	$\text{Ni}(\text{CO})_2(\text{C}_3\text{H}_6\text{O}_2)^+$	$\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{CO})_4^+$
206	$\text{Ni}(\text{C}_3\text{H}_6\text{O}_2)_2^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$, $\text{NiCO}(\text{C}_3\text{H}_6\text{O}_2)^+$
216	$\text{Ni}(\text{CO})_3(\text{C}_3\text{H}_6\text{O}_2)^+$	$\text{Ni}(\text{CO})_3^+$
234	$\text{NiCO}(\text{C}_3\text{H}_6\text{O}_2)_2^+$	$\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{CO})_4^+$ $\text{Ni}(\text{CO})_2(\text{C}_3\text{H}_6\text{O}_2)^+$

Here, the reactive organic species is $\text{C}_2\text{H}_4\text{O}^+$, which reacts with $\text{Ni}(\text{CO})_4$ to displace 3 CO's.

d. $\text{Ni}(\text{CO})_x^+$ reactions with 1,3-dioxane
 $(\text{C}_4\text{H}_8\text{O}_2)$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Ni}(\text{CO})_4$ and 1,3-dioxane are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursors(s)</u>
86	$\text{Ni}(\text{C}_2\text{H}_4)^+$	Ni^+
88	$\text{Ni}(\text{CH}_2\text{O})^+$	Ni^+ , NiCO^+
115	$\text{Ni}(\text{C}_3\text{H}_5\text{O})^+$	$\text{C}_3\text{H}_5\text{O}^+$
118	$\text{Ni}(\text{C}_2\text{H}_4\text{O}_2)^+$	NiCO^+
132	$\text{Ni}(\text{C}_3\text{H}_6\text{O}_2)^+$	NiCO^+

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
145	$\text{Ni}(\text{CO})_2(\text{OCH}_3)^+$	C_2H_5^+ , OCH_3^+
146	$\text{Ni}(\text{C}_4\text{H}_8\text{O}_2)^+$	Ni^+ , NiCO^+ , $\text{Ni}(\text{CO})_2^+$
160	$\text{NiCO}(\text{C}_3\text{H}_6\text{O}_2)^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
174	$\text{NiCO}(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
188	$\text{Ni}(\text{CO})_2(\text{C}_3\text{H}_6\text{O}_2)^+$	$\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{CO})_4^+$
202	$\text{Ni}(\text{CO})_2(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Ni}(\text{CO})_4^+$
220	$\text{Ni}(\text{C}_4\text{H}_8\text{O}_2)(\text{C}_3\text{H}_6\text{O}_2)^+$	NiCO^+ , $\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{C}_4\text{H}_8\text{O}_2)^+$
234	$\text{Ni}(\text{C}_4\text{H}_8\text{O}_2)^+$	NiCO^+ , $\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$ $\text{Ni}(\text{C}_4\text{H}_8\text{O}_2^+)$, $\text{NiCO}(\text{C}_4\text{H}_8\text{O}_2)^+$

Where m/e 115 and 145 are products arising from the $\text{C}_3\text{H}_5\text{O}^+$ and OCH_3^+ ion-molecule reactions with neutral $\text{Ni}(\text{CO})_4$.

e. $\text{Ni}(\text{CO})_x^+$ reactions with 1,4-dioxane
 $(\text{C}_4\text{H}_8\text{O}_2)$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Ni}(\text{CO})_4$ and 1,4-dioxane and p-dioxane- d_8 are listed in Table 10, with their precursors as identified by double resonance. Note that m/e 87 was formed by H atom abstraction by Ni^+ .

f. $\text{Ni}(\text{CO})_x^+$ reactions with 12-crown-4
 $(\text{C}_8\text{H}_{16}\text{O}_4)$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Ni}(\text{CO})_4$ and 12-crown-4 are listed below, with their precursors as identified by double resonances.

Table 10. $\text{Ni}(\text{CO})_4$ Reactions With p-Dioxane And p-Dioxane d_8

p-dioxane			p-dioxane d_8		
m/e	stoichiometry	precursor(s)	m/e	stoichiometry	precursor(s)
86	$\text{Ni}(\text{C}_2\text{H}_4)^+$	Ni^+	90	$\text{Ni}(\text{CD}_2\text{O})^+$	$\text{Ni}^+, \text{NiCO}^+$
87	NiH^+	$\text{Ni}^+, \text{NiCO}^+$		$\text{Ni}(\text{C}_2\text{D}_4)^+$	
88	$\text{Ni}(\text{CH}_2\text{O})^+$	$\text{Ni}^+, \text{NiCO}^+$	106	$\text{Ni}(\text{C}_2\text{D}_4\text{O})^+$	$\text{Ni}^+, \text{NiCO}^+$
102	$\text{Ni}(\text{C}_2\text{H}_4\text{O})^+$	$\text{Ni}^+, \text{NiCO}^+$	122	$\text{Ni}(\text{C}_2\text{D}_4\text{O}_2)^+$	$\text{Ni}^+, \text{NiCO}^+$
118	$\text{Ni}(\text{C}_2\text{H}_4\text{O}_2)^+$	$\text{Ni}^+, \text{NiCO}^+$	154	$\text{Ni}(\text{C}_4\text{D}_8\text{O}_2)^+$	$\text{Ni}^+, \text{NiCO}^+, \text{Ni}(\text{CO})_2^+$
146	$\text{Ni}(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Ni}^+, \text{NiCO}^+, \text{Ni}(\text{CO})_2^+$	182	$\text{NiCO}(\text{C}_4\text{D}_8\text{O}_2)^+$	$\text{Ni}(\text{CO})_2^+, \text{Ni}(\text{CO})_3^+$
174	$\text{NiCO}(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Ni}(\text{CO})_2^+, \text{Ni}(\text{CO})_3^+$		$\text{C}_4\text{D}_8\text{O}_2^+$	
202	$\text{Ni}(\text{CO})_2(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{C}_4\text{H}_8\text{O}_2^+$	210	$\text{Ni}(\text{CO})_2(\text{C}_4\text{D}_8\text{O}_2)^+$	$\text{Ni}(\text{CO})_3^+, \text{Ni}(\text{CO})_4^+$
		$\text{Ni}(\text{CO})_3^+, \text{Ni}(\text{CO})_4^+$	250	$\text{Ni}(\text{C}_4\text{D}_8\text{O}_2)_2^+$	$\text{Ni}(\text{CO})_2^+, \text{Ni}(\text{CO})_3^+$
		$\text{C}_4\text{H}_8\text{O}_2^+$			$\text{C}_4\text{D}_8\text{O}_2^+, \text{NiCO}(\text{C}_4\text{D}_8\text{O}_2)^+$
234	$\text{Ni}(\text{C}_4\text{H}_8\text{O}_2)_2^+$	$\text{Ni}(\text{CO})_2^+, \text{Ni}(\text{CO})_3^+$			
		$\text{C}_4\text{H}_8\text{O}_2^+, \text{NiCO}(\text{C}_4\text{H}_8\text{O}_2)^+$			

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
100	$\text{Ni}(\text{C}_2\text{H}_2\text{O})^+$	Ni^+ , NiCO^+ , $\text{Ni}(\text{CO})_2^+$
102	$\text{Ni}(\text{C}_2\text{H}_4\text{O})^+$	Ni^+ , NiCO^+
103	$\text{Ni}(\text{OC}_2\text{H}_5)^+$	$\text{C}_2\text{H}_5\text{O}^+$
118	$\text{Ni}(\text{C}_2\text{H}_4\text{O}_2)^+$	Ni^+ , NiCO^+ , $\text{Ni}(\text{CO})_2^+$
146	$\text{Ni}(\text{C}_4\text{H}_8\text{O}_2)^+$	NiCO^+ , $\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
157	$\text{NiCO}(\text{C}_2\text{H}_3\text{O})^+$	$\text{C}_2\text{H}_3\text{O}^+$
174	$\text{NiCO}(\text{C}_4\text{H}_8\text{O}_2)^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{CO})_4^+$
178	$\text{Ni}(\text{C}_5\text{H}_{12}\text{O}_3)^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
202	$\text{Ni}_2\text{CO}(\text{C}_2\text{H}_2\text{O}_2)^+$	Ni^+ , NiCO^+ , $\text{Ni}_2(\text{CO})_2^+$
204	$\text{Ni}_2\text{CO}(\text{C}_2\text{H}_4\text{O}_2)^+$	Ni^+ , NiCO^+ , $\text{Ni}_2(\text{CO})_2^+$
206	$\text{NiCO}(\text{C}_5\text{H}_{12}\text{O}_3)^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{CO})_4^+$
214	$\text{Ni}_2(\text{CO})_2(\text{C}_2\text{H}_2\text{O})^+$	Ni^+ , NiCO^+ , $\text{Ni}(\text{C}_2\text{H}_2\text{O})^+$
216	$\text{Ni}_2(\text{CO})_2(\text{C}_2\text{H}_4\text{O})^+$	Ni^+ , NiCO^+ , $\text{Ni}(\text{C}_2\text{H}_4\text{O})^+$
232	$\text{Ni}(\text{C}_8\text{H}_{14}\text{O}_4)^+$	Ni , NiCO^+
234	$\text{Ni}(\text{C}_8\text{H}_{16}\text{O}_4)^+$	NiCO^+ , $\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{CO})_4^+$

Note that $\text{C}_2\text{H}_5\text{O}^+$ is the most prominent ion in EI spectra of all crowns¹⁴⁹. The ions m/e 103, 157 are formed from $\text{C}_2\text{H}_5\text{O}^+$ and $\text{C}_2\text{H}_3\text{O}^+$ reactions with natural $\text{Ni}(\text{CO})_4$.

g. $\text{Ni}(\text{CO})_x^+$ reactions with 15-crown-5
 $(\text{C}_{10}\text{H}_{20}\text{O}_5)$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Ni}(\text{CO})_4$ and 15-crown-5 are listed below, with

their precursors as identified by double resonance technique.

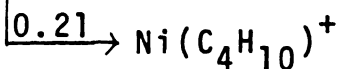
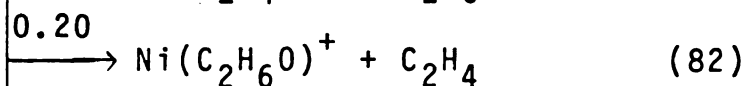
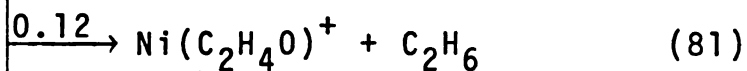
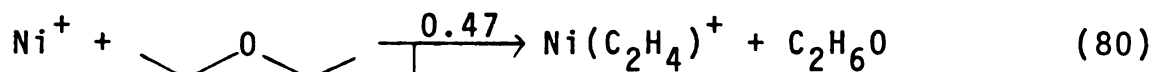
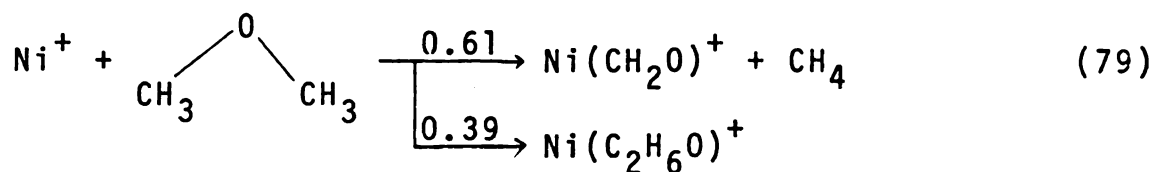
<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
118	$\text{Ni}(\text{C}_2\text{H}_4\text{O}_2)^+$	Ni^+ , NiCO^+
162	$\text{Ni}(\text{C}_4\text{H}_8\text{O}_3)^+$	Ni^+ , NiCO^+
190	$\text{Ni}(\text{C}_6\text{H}_{12}\text{O}_3)^+$	Ni^+ , NiCO^+
192	$\text{Ni}(\text{C}_6\text{H}_{14}\text{O}_3)^+$	NiCO^+
207	$\text{Ni}(\text{C}_6\text{H}_{13}\text{O}_4)^+$	Ni^+ , NiCO^+
278	$\text{Ni}(\text{C}_{10}\text{H}_{20}\text{O}_5)^+$	Ni^+ , NiCO^+ , $\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{CO})_4^+$

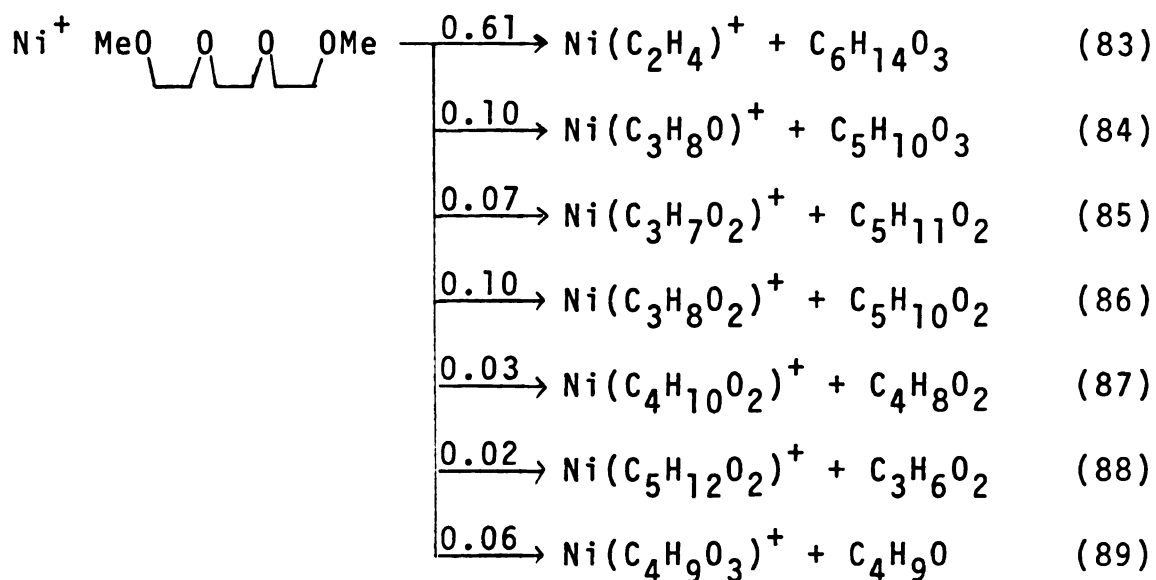
B. Discussion

1. Linear Ethers and Polyethers

a. Reactions of Ni^+

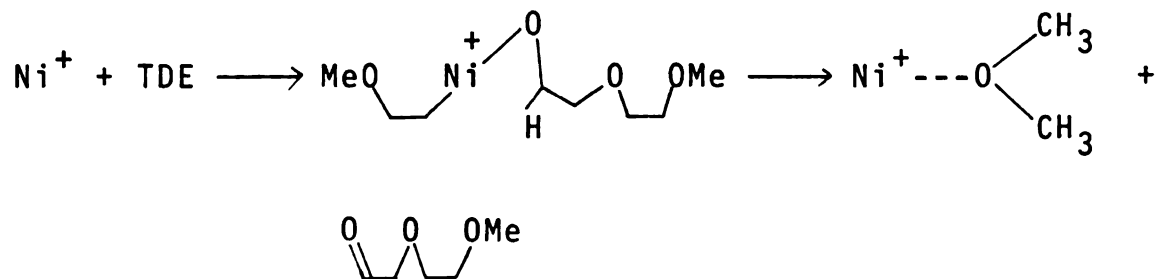
Ni^+ reactions with dimethylether, diethylether and TDE are summarized below:





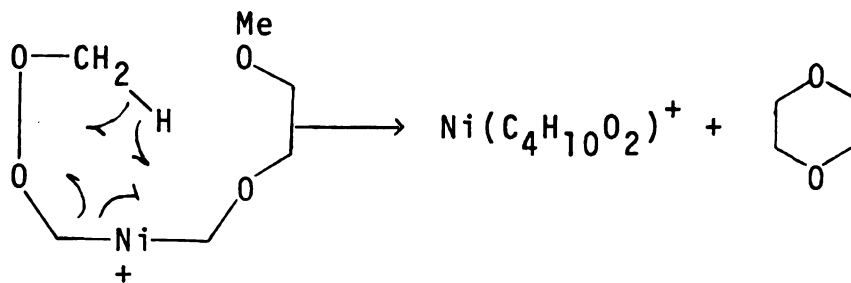
Products in reaction (79)-(82) are similar to those reported for Fe^+ . Note that $\text{Ni}(\text{CH}_2\text{O})^+$ doesn't undergo successive reaction. Also, Ni^+ can directly form an addition complex with diethylether. This may, perhaps, indicate that Ni^+ has a weaker complexation energy with oxygen in ethers than Fe^+ or Cr^+ .

Products in (83), (85), (86) and (88) can be explained similarly to that of Cr^+ in (48)-(50) except that no β -H shifts in (85). It may shift but be retained on the metal center. The product in (84) can be explained in a similar way:

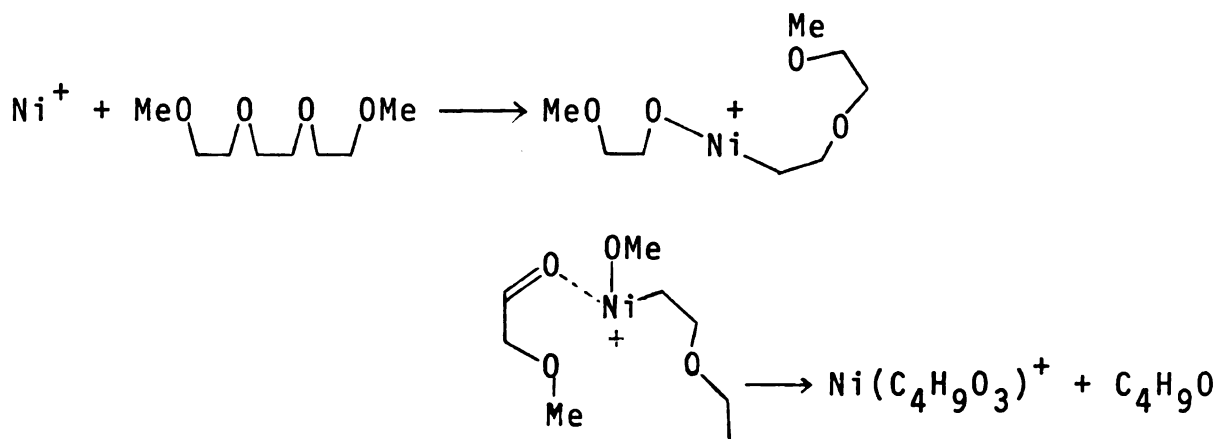


The product in (87) might be formed similarly to that

in (83):

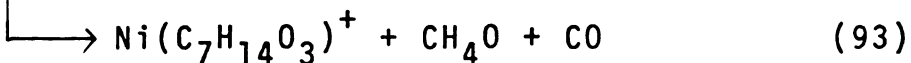
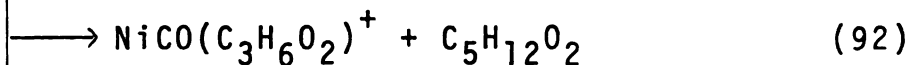
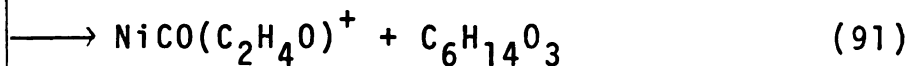
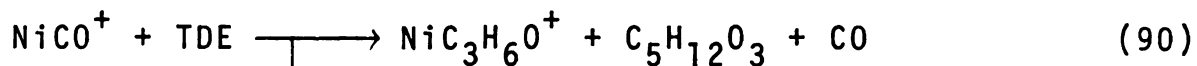


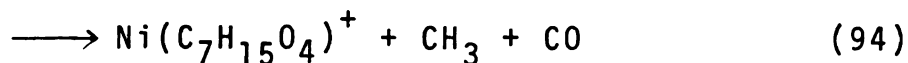
The product in (89) is hard to explain. One possibility is that Ni^+ inserts in a stepwise manner into C-O bonds between skeletal atoms (5,6) and (10,11):



b. Reactions of NiCO^+

NiCO^+ reactions with diemthylether and diethylether only result in substitution and successive reactions. NiCO^+ reacts with TDE yielding some new products:

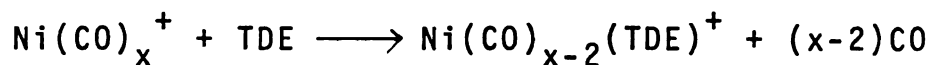




Products in (90 and (92) follow the same mechanism as that in (84) and (86) except that the β -H shift occurs from the "other" side after Ni^+ inserts into C-O bonds. In both cases, CO acts as a spectator with and without concurrent loss of CO in (90) and (92) respectively.

The product in (91) is 28 mass units above $\text{Ni}(\text{C}_2\text{H}_4\text{O})^+$, however, the incorporation of CO might be an indication of a different mechanism, because it makes a β -H shift available for shifting after NiCO^+ inserts between skeletal atoms 3 and 4. Similarly, the product in (93) can be explained by Ni^+ insertion into the C-O (skeletal atoms 10 and 11), followed by a β -H shift. The formation of $\text{Ni}(\text{C}_7\text{H}_{15}\text{O}_4)^+$ is a high energy process, i.e. once Ni^+ inserts into the CH_3 -O bond, it eliminates the $\cdot\text{CH}_3$ radical.

$\text{Ni}(\text{CO})_x^+$ reactions with diemthylether, diethylether and TDE only are substitution reactions. However, one important result has to be mentioned here:



$$x = 2, 3, 4$$

Hence, the formation of the $\text{Ni}(\text{TDE})^+$ adduct ion is different from what we have seen in the Fe^+ and Cr^+ cases where the interactions between the metal center and oxygen

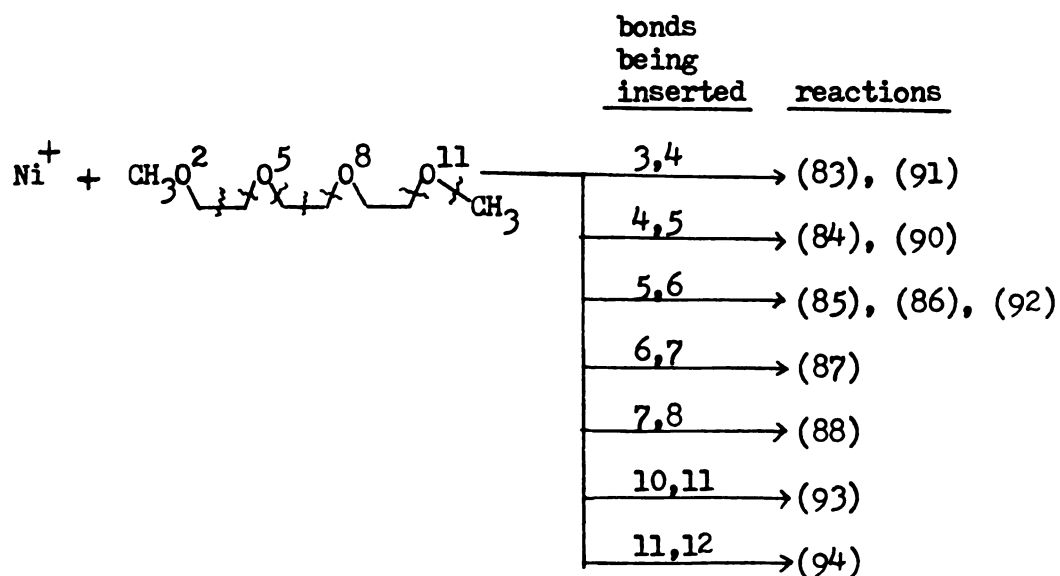
atoms (or $-\text{CH}_2-$) are so strong that both Fe^+ and Cr^+ easily induce fragmentations.

From Table 2, it is known that the bond energies of Ni^+ to oxygen, a methyl group and hydrogen are small ($D(\text{Ni}-\text{O}) \approx 45$ kcal/mole, $D(\text{Ni}^+-\text{CH}_3) \approx 49$ kcal/mole and $D(\text{Ni}^+-\text{H}) \approx 43$ kcal/mole) so that it can form an addition complex and randomly insert into any C-O or C-C bond in TDE as shown in Scheme XXVI.

Also, the odd mass products corresponding to either no β -H shift or H atom retention by the metal were observed in the reactions of Ni^+ and TDE.

The Ni^+ and NiCO^+ reactions with TDE can be summarized in Scheme XXVI (the numbers on the arrow bar are the skeletal atoms of TDE and are used to indicate the bond into which Ni^+ inserts to yield reaction products).

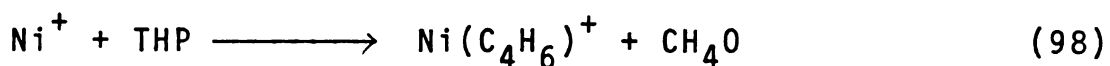
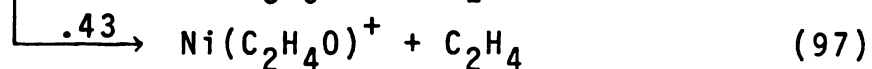
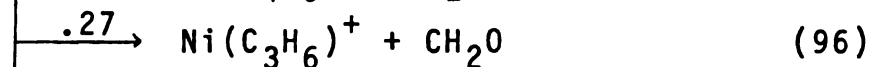
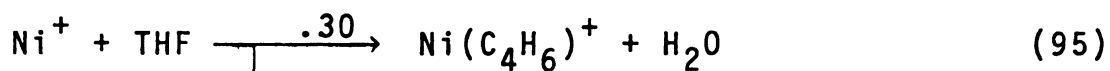
Scheme XXVI.



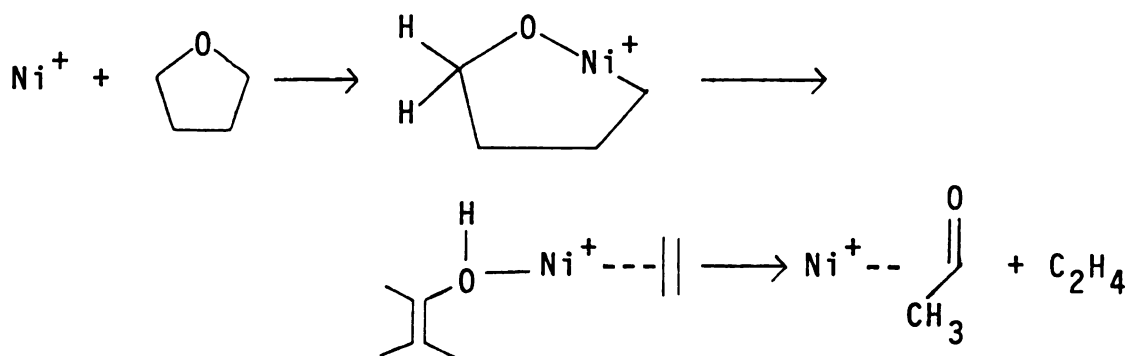
2. Cyclic Ethers

a. Ni⁺ reactions with THF and THP

The Ni⁺ reactions with THF and THP are summarized below:



Products in (95), (96) and (98) are similar to those observed for Fe⁺. However, the product in (97), Ni(C₂H₄O)⁺, is a new product, and can be explained as follows:



Note that the enol ligand might rearrange to keto form which is more stable.

b. Ni(CO)_x^+ reactions with THF and THP

As the number of CO's present on the metal increases, ligand substitution becomes the predominant process.

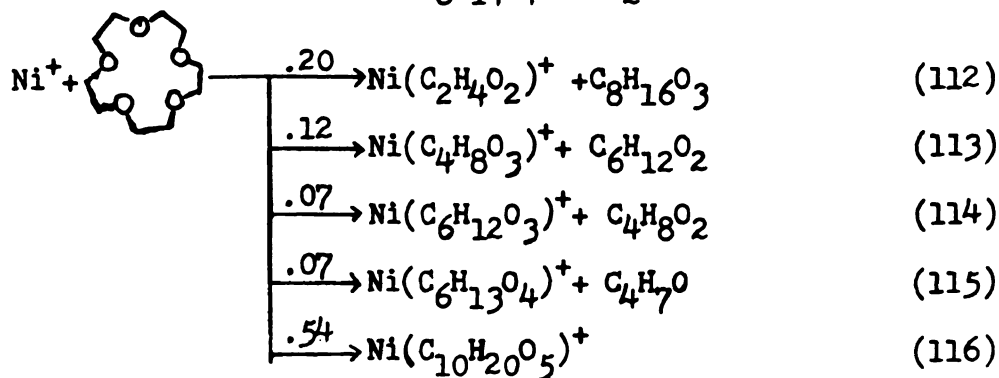
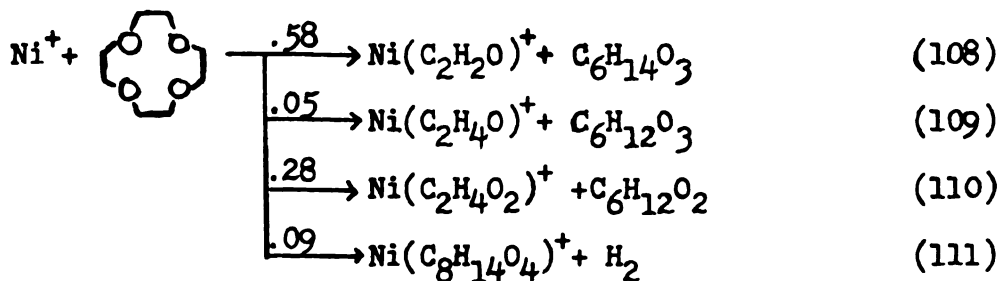
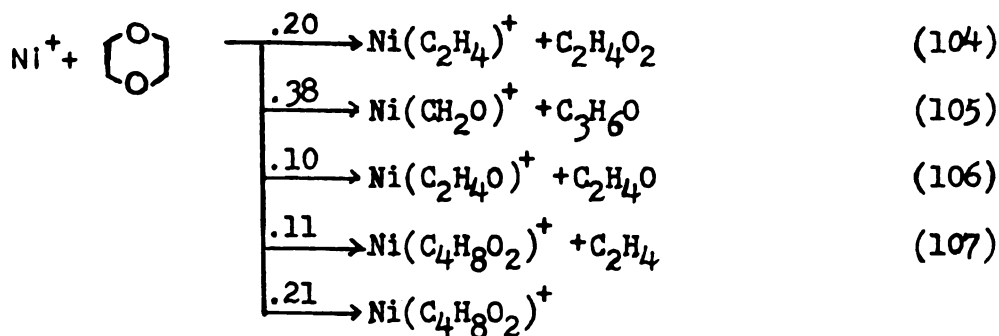
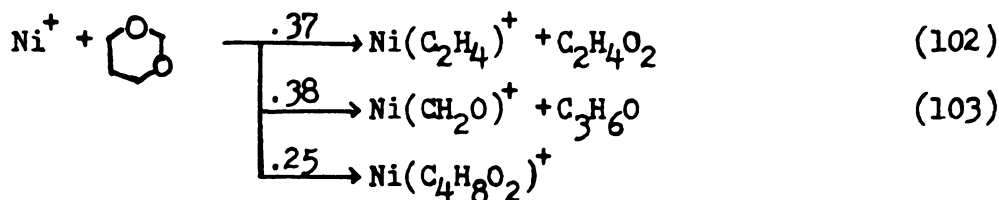
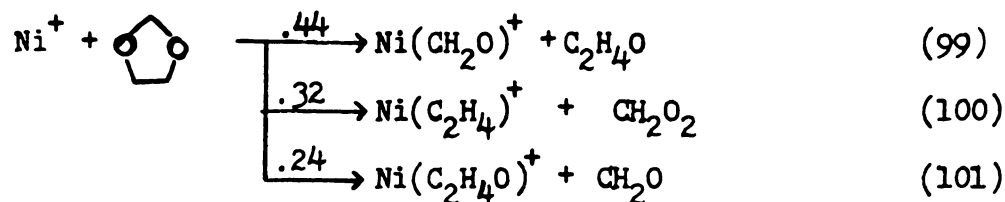
3. Cyclic Polyethers

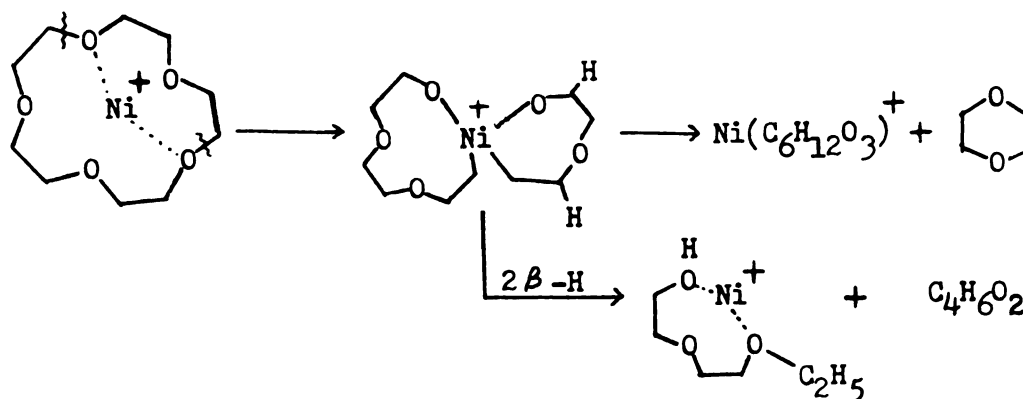
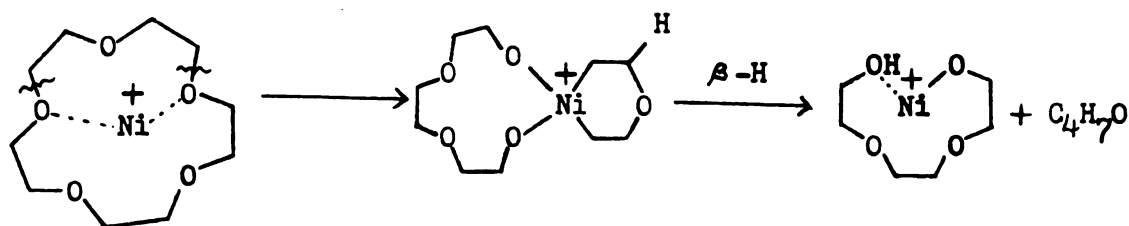
a. Ni^+ reactions

Ni^+ reactions with 1,3-dioxolane, 1,3-dioxane, p-dioxane (d_8), 12-crown-4 and 15-crown-5 are listed in Table 11.

Again, most reaction products have been observed in the reactions of Fe^+ with 1,3-dioxolan, 1,3-dioxane, p-dioxane and 12-crown-4 except that $\text{Ni(C}_2\text{H}_4\text{O)}^+$ is present in the reactions (106) and (109). Presumably, the formation of $\text{Ni(C}_2\text{H}_4\text{O)}^+$ in reactions (101), (106) and (109) follows the same mechanism as was explained in Scheme XII. Note that Ni^+ also reacts with 12-crown-4 to give $\text{Ni(C}_8\text{H}_{14}\text{O}_4)^+$ with an elimination of one molecule of H_2 as shown in reaction (111). This result implies that Ni^+ actually interacts with one or two oxygen atoms only, and then inserts into a C-O bond, followed by the β -H shift.

Products in (112) and (113) are similar to that observed for Fe^+ as shown in Scheme XV and XVII. Products in (114) and (115) can be explained in terms of Scheme XXVII and XXVIII.

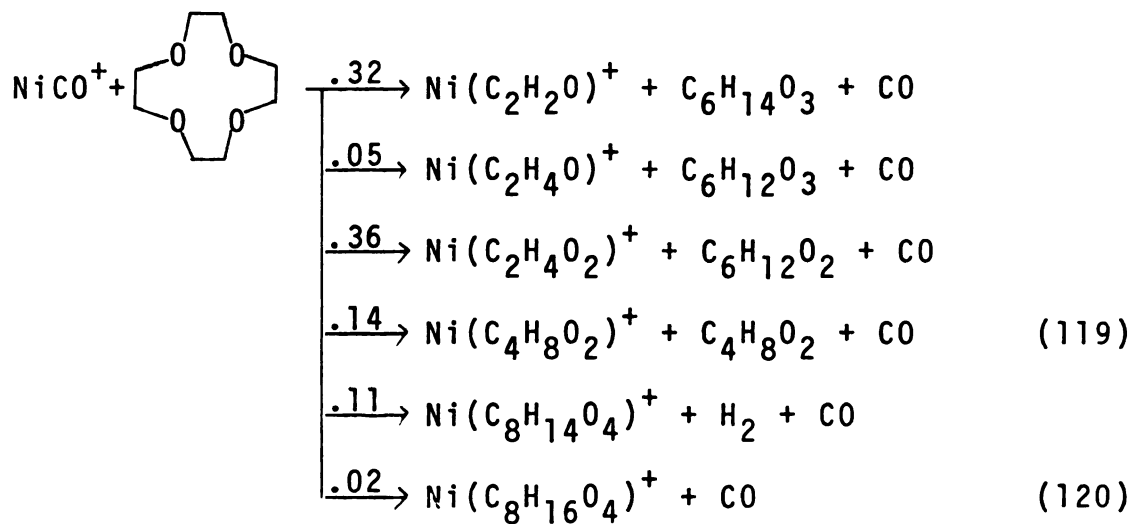
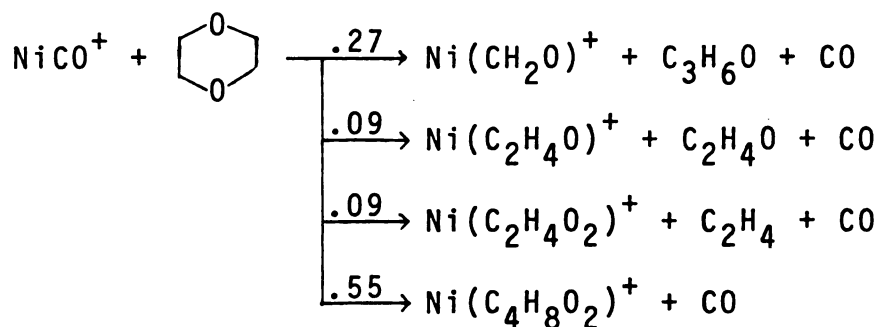
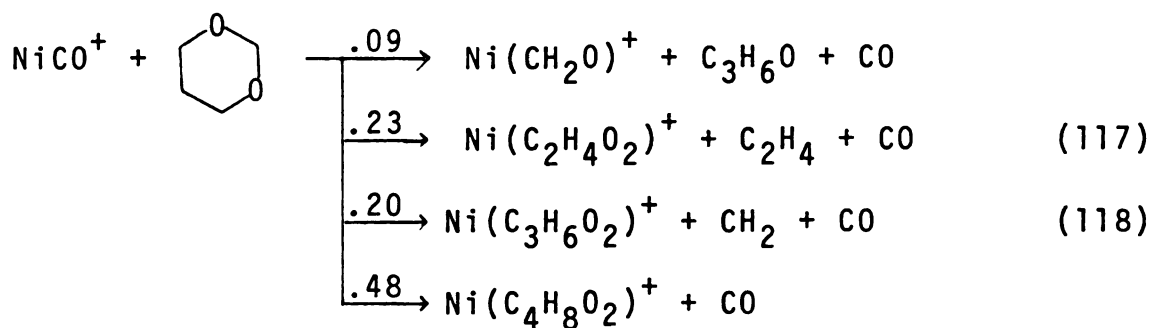
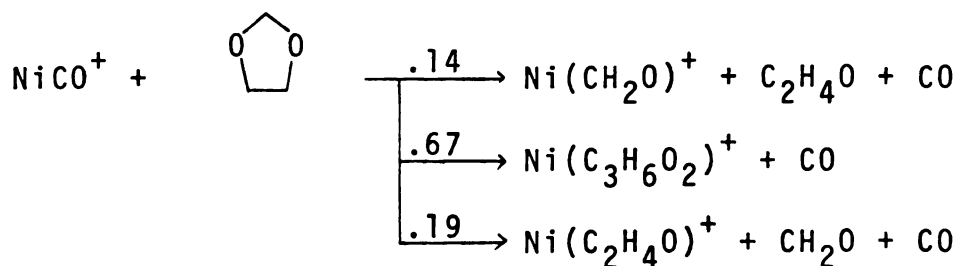
Table 11. Ni^+ Reactions With Cyclic Polyethers

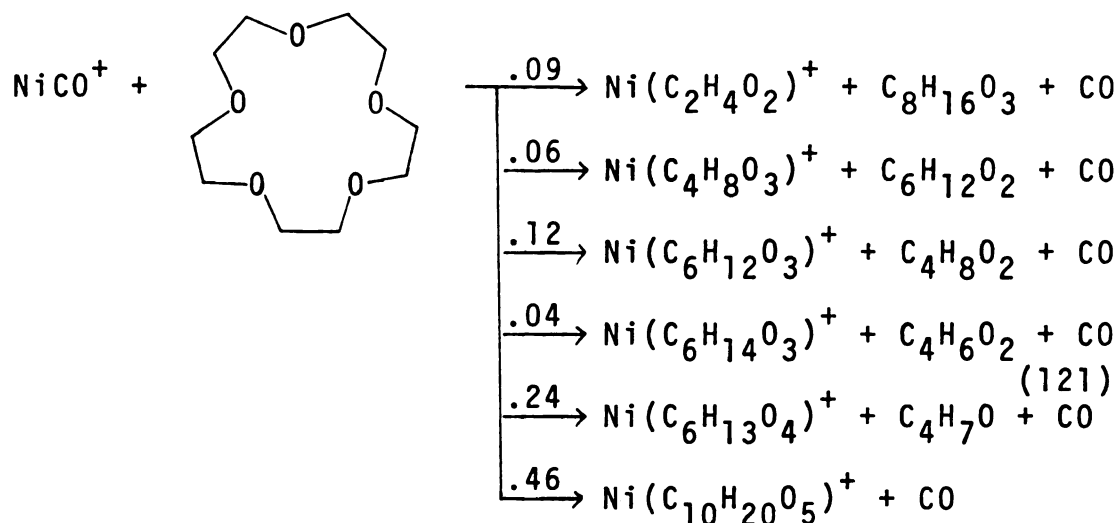
Scheme XXVIIScheme XXVIII

The formation of the adduct ion, $\text{Ni}(\text{C}_{10}\text{H}_{20}\text{O}_5)^+$ might indicate that Ni^+ interacts with one or two oxygens in the crown and since their interactions are not so strong, fragmentation does not occur.

b. NiCO^+ reactions

NiCO^+ reactions with 1,3-dioxolan, 1,3-dioxane, p-dioxane, 12-crown-4 and 15-crown-5 are summarized below:



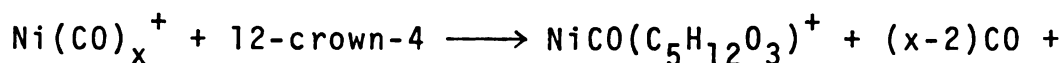
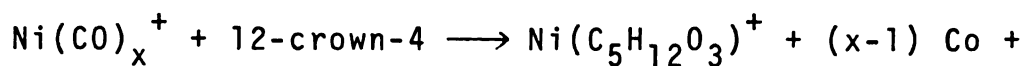


Reactions (117)-(121) are "new" (not previously observed) reactions. Products in (117), (119) can be explained in a manner similar to what was discussed for Fe^+ as shown in Scheme XII. These two product ions ($\text{NiC}_2\text{H}_4\text{O}_2^+$ and $\text{NiC}_4\text{H}_8\text{O}_2^+$) do not have Ni^+ as a precursor. Apparently, when Ni^+ complexes with a polyether, the interaction energy is sufficient to induce certain fragmentations. When the reactant is NiCO^+ , the energy "deposited" into the polyether varies, since the cleavage of the M-CO^+ bond can compete for the available energy. The same reason is also applicable concerning the formation of the adduct ion, $\text{Ni}(\text{C}_8\text{H}_{16}\text{O}_4)^+$ in reaction (120). The product ion in (121) can be explained by the mechanism in Scheme XXVII.

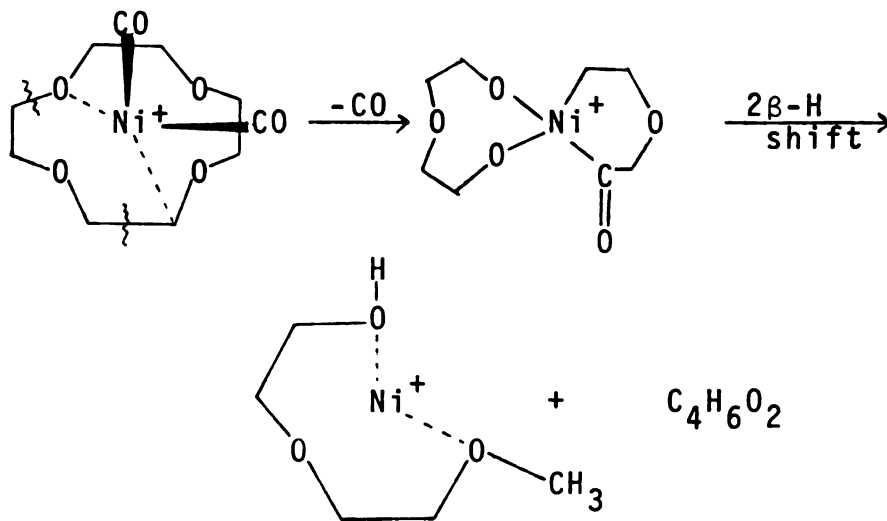
c. $\text{Ni}(\text{CO})_x^+$ reactions

The reactions of $\text{Ni}(\text{CO})_x^+$ ($x = 2-4$) with 1,3-dioxolan, 1,3-dioxane and p-dioxane are only substitution reactions. $\text{Ni}(\text{CO})_2^+$ and $\text{Ni}(\text{CO})_3^+$ react with 12-crown-4 to give "new"

products, $\text{Ni}(\text{C}_5\text{H}_{12}\text{O}_3)^+$ and $\text{NiCO}(\text{C}_5\text{H}_{12}\text{O}_3)^+$:



These two products can be understood in terms of the structure as shown in Scheme XII (p. 74), in which the Ni^+ will interact with oxygen atom #1 and carbon atom #5 as shown below:



It is of interest to note that both 12-crown-4 and 15-crown-5 can displace up to 4CO's from Ni^+ . If the reactions are induced from the cavity center, CO ligands on Ni^+ will prevent it from getting close to all of the crown's oxygen atoms.

4. Thermodynamic Conclusions

Table 12 lists all neutrals lost in the $\text{Ni}(\text{CO})_x^+$ reactions with all ethers discussed above and their branching ratios.

Dimethylether can displace one CO from Ni^+ , and diethylether can displace two CO's from Ni^+ , suggesting that $6.58 \text{ kcal/mole} < D(\text{Ni}^+-\text{Me}_2\text{O}) < 71.17 \text{ kcal/mole}$. Similarly, for diethylether, $71.17 \text{ kcal/mole} < D(\text{Ni}^+-\text{Et}_2\text{O}) < 101.74 \text{ kcal/mole}$.

In comparison with the complexation energy of Fe^+ , Ni^+ has a smaller complexation energy. Thus, we did not observe $\text{Ni}(\text{C}_4\text{H}_8\text{O})^+$ as a product in the reaction of Ni^+ with diethylether, since less energy is available. Such an analysis in the reactions with cyclic ethers and polyethers may not be useful, since orbital comparability, orientation in space and many other factors are involved. Both THF and THP can displace up to two CO's from Fe^+ and Ni^+ , but only one product is observed in the reaction of Ni^+ with THP, (which produced three products in the case of Fe^+). In contrast, Ni^+ forms three products in its reaction with THF, (which also forms three with Fe^+). The difference is that although both compounds can displace up to 2CO's from both Fe^+ and Ni^+ , the bare Ni^+ does not contribute to the formation of the addition complex. This in turn relates to the bonding of ligands to the metal center and the orbitals used by the metal center, etc.

Table 12. Neutrals Lost In The Reactions Of $M1(OO)^+$ With Ethere

			THE						12-crown-4	15-crown-5
$M1^+$	CH_3^+OO (.61) AC (.39)	$C_2H_5^+OO$ (.47) $C_2H_6^+$ (.12) C_2H_6 (.20) AC (.21)	$C_6H_{10}O_3$ (.61) $C_5H_{10}O_3$ (.10) $C_5H_{11}O_2$ (.07) $C_5H_{10}O_2$ (.10) $C_6H_9O_2$ (.03) $C_5H_9O_2$ (.06)	CH_3O (.27) H_2O (.30) C_2H_5 (.43)	CH_3O (.32) C_2H_5O (.44) CH_2O (.24)	$C_2H_5O_2$ (.37) C_2H_6O (.38) H_2O (.25) AC (.21)	$C_2H_5O_2$ (.20) C_2H_6O (.38) C_2H_5O (.10) C_2H_6 (.11) AC (.21)	$C_6H_{10}O_3$ (.58) $C_6H_{12}O_3$ (.05) $C_6H_{12}O_2$ (.28) $C_6H_8O_2$ (.07) C_6H_9O (.09) AC (.54)		
$M1(OO)^+$	CH_3^+OO (.39) OO (.61)	$C_2H_6^+OO$ (.10) $C_2H_5^+OO$ (.27) OO (.63)	$C_5H_{12}O_3^+OO$ (.05) $C_5H_{10}O_3^+OO$ (.08) $C_6H_{10}O_3$ (.14) $C_5H_{11}O_2^+OO$ (.02) $C_5H_{10}O_2^+OO$ (.15) $C_6H_9O_2^+OO$ (.02) $C_5H_9O_2^+OO$ (.04) $C_6H_9O^+OO$ (.04) CH_3O^+OO (.04) CH_3^+OO (.40)	CH_3O^+OO (.07) $C_2H_5^+OO$ (.09) H_2O^+OO (.12) OO (.72)	$C_2H_5O^+OO$ (.14) CH_2O^+OO (.19) OO (.67)	$C_2H_5O^+OO$ (.09) $C_2H_6^+OO$ (.23) CH_2^+OO (.20) OO (.48)	$C_2H_5O_2^+OO$ (.27) $C_2H_6O^+OO$ (.09) $C_2H_5^+OO$ (.09) OO (.55)	$C_6H_{10}O_3^+OO$ (.32) $C_6H_{12}O_3^+OO$ (.05) $C_6H_{12}O_2^+OO$ (.36) $C_6H_8O_2^+OO$ (.14) $C_6H_9O^+OO$ (.11) H_2O (.02) OO (.46)		
$M1(OO)_2^+$	OO	200 OO	$C_5H_{12}O_3^+OO$ (.09) $C_5H_{10}O_3^+OO$ (.07) $C_5H_{11}O_2^+OO$ (.07) CH_3O^+OO + 200 (.07) CH_3^+OO + 200 (.16) 200 (.62)	200 OO	200 OO	200 (.21) CH_2 OO (.09) OO (.70)	200 OO	$C_6H_{10}O_3^+OO$ (.09) $C_6H_{12}O_3^+OO$ (.22) $C_6H_8O_2^+OO$ + 200 (.36) $C_6H_9O_2^+OO$ + OO (.07) $C_5H_9O^+OO$ + 200 (.16) $C_5H_9O^+OO$ + OO (.06)	200	
$M1(OO)_3^+$	OO	200 100	$C_5H_{12}O_3^+OO$ (.13) $C_5H_{10}O_3^+OO$ (.05) $C_5H_{11}O_2^+OO$ (.02) CH_3O^+OO + 300 (.07) CH_3^+OO + 300 (.73)	200 100	200 100 AC	CH_2 200 (.1) 210 (.81) CH_2^+OO (.09)	200 100	$C_6H_{10}O_3^+OO$ (.34) $C_6H_8O_2^+OO$ + 200 (.28) $C_5H_9O^+OO$ + 300 (.19) $C_5H_{10}O^+OO$ + 200 (.15) 300 (.06)	200	
$M1(OO)_4^+$		200	$C_5H_{12}O_3^+OO$ (.06) CH_3O^+OO + 400 (.08) 400 (.86)	200	200	200 (.9) CH_2^+OO + 200 (.1)	200	$C_6H_8O_2^+OO$ + 300 (.59) $C_5H_9O^+OO$ + 300 (.30) 400 (.11)	400	

In the case of polyethers, the thermodynamics conclusions are more difficult to make. The rough estimation of complexation energy for Ni^+ with TDE, 12-crown-4 and 15-crown-5 will be greater than 126.32 kcal/mole. It is unclear how many M^+-O interactions this figure reflects.

Obviously, many more experiments have to be conducted for an understanding of metal ion-polyether interactions. Metal ion reactions with multifunctional molecules are somewhat an interface between molecular and bulk interactions. Although the explanation of product ions is somewhat speculative, this is the first attempt to carry out this kind of study. Other attempts still have to be tried on smaller molecules to determine other factors controlling the formation and distribution of products. Section 5 is an attempt to do this.

IV. Comparison Of $\text{Fe}(\text{CO})_x^+$, $\text{Cr}(\text{CO})_x^+$ And $\text{Ni}(\text{CO})_x^+$ In Their Reactions With Ethers.

Table 13 summarizes the ether reactions for Cr^+ , Fe^+ and Ni^+ , (excluding successive reactions and complexation reactions). By consulting Table 6, Table 9 and Table 12, it is readily seen that, as the number of CO's on the metal center increases, the "reactivity" decreases and only substitution reactions are observed.

In the reaction of Fe^+ , a clear macrocyclic effect is observed, namely the number of products changes dramatically

Table 13. Number Of Reaction Products Observed For Metal
Centers In Various States Of Coordination.*

Reactant Ion	$\text{CH}_3\text{O}^-\text{CH}_3$			$\text{V} \sim \text{O} \sim \text{V}$			TDE								
M^+	0	1	1	1	3	3	1	7	0	2	3	1	3	1	1
MCO^+	0	0	1	1	3	2	2	11	0	2	3	1	0	0	0
$\text{M}(\infty)_2^+$	0	0	0	0	1	0	6	6	0	0	0	0	0	0	0
$\text{M}(\infty)_3^+$	0	0	0	0	0	0	5	5	0	0	0	0	0	0	0
$\text{M}(\infty)_4^+$	0	0	0	0	0	0	4	3	0	0	0	0	0	0	0
$\text{M}(\infty)_5^+$	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
$\text{M}(\infty)_6^+$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\text{M}^+ =$	Cr	Fe	Ni	Cr	Fe	Ni	Cr	Fe	Ni	Cr	Fe	Ni	Cr	Fe	Ni

* Does not include successive reaction products and complexation products

from linear polyethers to cyclic polyethers. THF and THP do not produce as many products as diethylether, due to their geometrical constraints, possibly leading to insufficient orbital overlap. Hence, $\text{Fe}(\text{CO})_2^+$ is still reactive in the reaction with diethylether and unreactive in its reaction with THF and THP. However, in its reactions with polycyclic ethers, Fe^+ starts to interact with multifunctional atoms to induce more products from the cavity center, exhibiting macrocyclic effect with 12-crown-4. When the ring size increases, this effect is decreased slightly and we expect that the reactions may be more like those observed linear polyethers in the reactions with 18-crown-6 and 21-crown-7 with Fe^+ inducing products more randomly, presumably due to its incapability of interacting with all functional atoms at a time. It is of interest to note that in the reactions with small polycyclic ethers, the $\text{Fe}(\text{CO})_x^+$ ions ($x \geq 2$) are unreactive, possibly implying that geometrical restrictions are present, although the initial interaction could be strong. Moreover, in the 12-crown-4 and 15-crown-5 systems, the addition complexes were not observed. Also, no substitution reactions occurred, suggesting that Fe^+ interacts with all oxygen atoms in the former and 3 or 4 oxygen atoms in the latter and the interaction must be very strong to undergo prompt fragmentations. It also implies that Fe^+ induces reactions from the cavity center or very close to it. Consequently, as more CO's are present on Fe^+ , it can no longer

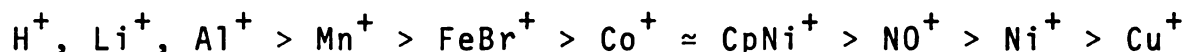
get close to the cavity center of 12-crown-4. Note that we also see some ligand effects, in which CO can act as either a spectator or a participator to give new products which are not seen in the ligand-free metal ion's case, especially in the TDE reaction.

The above model can also be applied to Cr^+ reactions with the knowledge that Cr^+ prefers to retain bonds to oxygen. Note that the formation of $\text{Cr}(\text{12-crown-4})^+$ may not be the result of the interaction of Cr^+ with 4 oxygen atoms from the cavity center, because it will result in fragmentation, due to its strong interaction with oxygen atoms. Instead, it could be the result of interaction with two oxygen atoms as in p-dioxane. Again, we have no evidence that Cr^+ could interact with all 5 oxygen atoms in 15-crown-5. The failure of Cr^+ to form an addition complex with 15-crown-5 could be due to the insufficient orbital overlaps. Also note that CO ligands play an important role in the reaction of this metal with TDE (see Table 9).

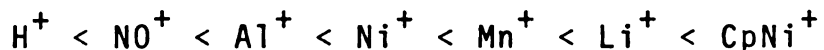
Since Ni^+ has relatively weak bond energies to oxygen and alkyl groups, the interaction between it and ether oxygen atoms is weak. Thus, we don't see the macrocyclic effect in this case. From Table 12, it is seen that NiCO^+ produces more products than Ni^+ . Ni^+ "randomly" interacts with the oxygen atoms in TDE to give many products. However, when the reactant cyclic polyether is 12-crown-4, it only produces 3 small molecular products, with another

product having one H_2 elimination. It appears that Ni^+ only interacts with orbitals in close proximity, possibly implying that the smaller size d-orbitals are used. Formation of addition complex of Ni^+ with TDE, 12-crown-4 and 15-crown-5 may indicate that Ni^+ is unable to interact strongly with many oxygen atoms because of its low bonding energy and that Ni^+ can't efficiently overlap with orbitals which are far from it.

Another way to look at the product distributions is from Staley's bond dissociation energy studies for two ligands in the gas phase¹⁵⁸⁻¹⁶². Staley found that metal ions are softer (based on HSAB theory) across the Periodic Table in the following order:



They also found that the bonding distance of interacting center of ligands to the metal ions is increasing in the following order:



Hence, we expect that Cr^+ prefers to retain harder acids such as oxygen acids with higher O/C ratios than Fe^+ does. Ni^+ prefers to retain softer acids with lower O/C ratio or simply alkenes. On the other hand, the shorter bonding distance will reflect a larger tendency to retain larger ligands and show a greater substituent effect.

Unfortunately, the experimental data is not sufficient yet to be used here.

5. Trends in First Row Transition Metal Ions In Gas Phase Reactions With Organic Molecules

In this work, $\text{Co(C)}_3\text{NO}$, Cr(CO)_6 , Ni(CO)_4 , Mo(CO)_6 and W(CO)_6 were obtained from Alfa products. Fe(CO)_5 and cis-2-pentene were obtained from Aldrich Chemical Company. 1-hexene, 2-pentanone and sec-butylamine were obtained from Chem Service. Iso-propyl chloride and propane gases were obtained from Matheson Gas Products Inc. Methyl iodide was obtained from MCB manufacturing Chemical Co., Inc. All compounds were used without further purification except cis-2-pentene which was distilled for 8 hours before use. All compounds were subject to standard freeze-pump-thaw cycles before use.

A number of papers have appeared in the literature on the chemistry of metal ions with organic molecules. Most of these papers have discussed one metal. No attempt has been made to discuss the reasons why different first row transition metals behave so differently with simple organic molecules. The decision was made to "target" some organic molecules whose reactivity may provide insights into the differences of metal ions. A number of factors which contribute to the chemistry observed in gas phase organometallic reactions should include:

1. The number of available low lying empty orbitals on the metal ions available for reaction. (For example, Hg^+ ($s^1 d^{10}$) can have two sp hybrid orbitals but $\text{Li}(s^2)$ cannot.)

2. Orientation and size of available orbitals of metal ions.

3. "Compatibility" of orbitals. For an insertion process to occur, bond lengths and bond angles in the initial metal-ligand complex must be compatible.

4. Thermodynamics (e.g., heats of formation, bond strength, promotion energy of metal ions (redistribution of electronic configuration)).

5. Orbital symmetry of the intermediates.

6. Electronic states of metal ions participating the reactions.

7. Kinetic factor (to be detected in ICR, the rate constant has to be in $10^{-9} - 10^{-11} \text{ cm}^3/\text{molecule/s}$).

The initial strategy in this work was as follows:

- a. Test if a metal ion inserts into the $\text{CH}_3\text{-I}$ bond.
- b. If a metal ion inserts, then test if there is $\beta\text{-H}$ shift across the metal center by studying reactions with $i\text{-C}_3\text{H}_7\text{Cl}$.
- c. Test if 5 or 6 membered ring intermediates are preferred by investigating metal ion/molecule reactions with 1-hexene, cis-2-pentene and 2-pentanone.

- d. Test if the metal ions react with nonpolar compounds such as propane, to estimate $D(M^+-alkyl)$.
- e. Test if the metal ions react with amines to determine the bond strength of the M^+-NR_2 bond.

These experiments were performed with a number of 1st row transition metal ions.

I. Reactions With Propane (C_3H_8)

A. Results

1. $Fe(CO)_x^+$ reactions with propane

Ions formed as products of ion-molecule reactions in a mixture of $Fe(CO)_5$ and C_3H_8 are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
84	$Fe(C_2H_4)^+$	Fe^+
98	$Fe(C_3H_6)^+$	Fe^+ , $FeCO^+$
100	$Fe(C_3H_8)^+$	$FeCO^+$
128	$FeCO(C_3H_8)^+$	$Fe(CO)_2^+$
153	$Fe(CO)_2C_3H_5^+$	$C_3H_5^+$
169	$Fe(CO)_4H^+$	$C_2H_4^+$, $C_2H_5^+$, $C_3H_8^+$
	and $Fe(CO)_3C_2H_5^+$	
181	$Fe(CO)_3C_3H_5^+$	$C_2H_5^+$, $C_3H_5^+$, $C_3H_7^+$
183	$Fe(CO)_3C_3H_7^+$	$C_2H_5^+$, $C_3H_7^+$
197	$Fe(CO)_5H^+$	$C_2H_5^+$, $C_3H_7^+$
	and $Fe(CO)_4C_2H_5^+$	

Note that $C_2H_5^+$, $C_3H_5^+$ and $C_3H_7^+$ are reactive organic species, especially $C_3H_5^{+168}$, which reacts with natural $Fe(CO)_5$, displacing two or three CO's.

2. $Co(CO)_x(NO)_y^+$ reactions with propane.

Ions formed as products of ion-molecule reactions in a mixture of $Co(CO)_3NO$ and C_3H_8 are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
87	$Co(C_2H_4)^+$	Co^+
101	$Co(C_3H_6)^+$	Co^+ , $CoCO^+$
103	$Co(C_3H_8)^+$	$CoCO^+$
118	$CoNOC_2H_5$	$C_2H_5^+$
130	$CoNOC_3H_5^+$	$C_3H_5^+$
131	$CoCO(C_3H_8)^+$	$Co(CO)_2^+$
133	$CoNO(C_3H_8)^+$	$CoNO^+$
146	$Co(CO)_2NOH^+$	$C_2H_5^+$, $CoCO^+$
158	$CoCONOC_3H_5^+$	$C_3H_5^+$
160	$CoCONOC_3H_7^+$	$C_3H_7^+$
174	$Co(CO)_3NOH^+$	$C_2H_5^+$, $CoCO^+$
188	$Co(CO)_2NOC_3H_7^+$	$C_3H_7^+$

3. $Ni(CO)_x^+$ reactions with propane

Ions formed as products of ion-molecule reactions in a mixture of $Ni(CO)_4$ and C_3H_8 are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
86	$\text{Ni}(\text{C}_2\text{H}_4)^+$	Ni^+
100	$\text{Ni}(\text{C}_3\text{H}_6)^+$	Ni^+ , NiCO^+
102	NiC_3H_8^+	NiCO^+
115	$\text{Ni}(\text{CO})_2\text{H}^+$	C_2H_5^+
127	$\text{NiCOC}_3\text{H}_5^+$	C_3H_5^+
130	$\text{NiCO}(\text{C}_3\text{H}_8)^+$	$\text{Ni}(\text{CO})_2^+$, C_3H_8^+
143	$\text{Ni}(\text{C}_3\text{H}_8)(\text{C}_3\text{H}_5)^+$	C_3H_8^+ , Ni^+ , NiCO^+
145	$\text{Ni}(\text{CO})_3\text{H}^+$	C_2H_5^+ , Ni^+ , NiCO^+
155	$\text{Ni}(\text{CO})_2\text{C}_3\text{H}_5^+$	C_3H_5^+
157	$\text{Ni}(\text{CO})_2\text{C}_3\text{H}_7^+$	C_3H_5^+ , C_3H_7^+ , $\text{NiCO}(\text{C}_3\text{H}_8)^+$
159	$\text{NiCO}(\text{C}_3\text{H}_8(\text{C}_2\text{H}_5))^+$	C_3H_7^+ , $\text{NiCO}(\text{C}_3\text{H}_8)^+$
186	$\text{Ni}(\text{CO})_3\text{C}_3\text{H}_8^+$	Ni^+

The ion at m/e 100 has a very small peak intensity compared with that of the comparable product for Co^+ , but it is similar to that observed for Fe^+ .

4. $\text{Cr}(\text{CO})_x^+$ reactions with propane

Ions formed as products of ion-molecule reactions in a mixture of $\text{Cr}(\text{CO})_6$ and C_3H_8 are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
80	$\text{Cr}(\text{C}_2\text{H}_4)^+$	Cr^+ , CrCO^+
96	$\text{Cr}(\text{C}_3\text{H}_8)^+$	CrCO^+
124	$\text{CrCO}(\text{C}_3\text{H}_8)^+$	CrCO^+

5. Mo(CO)_x^+ reactions with propane.

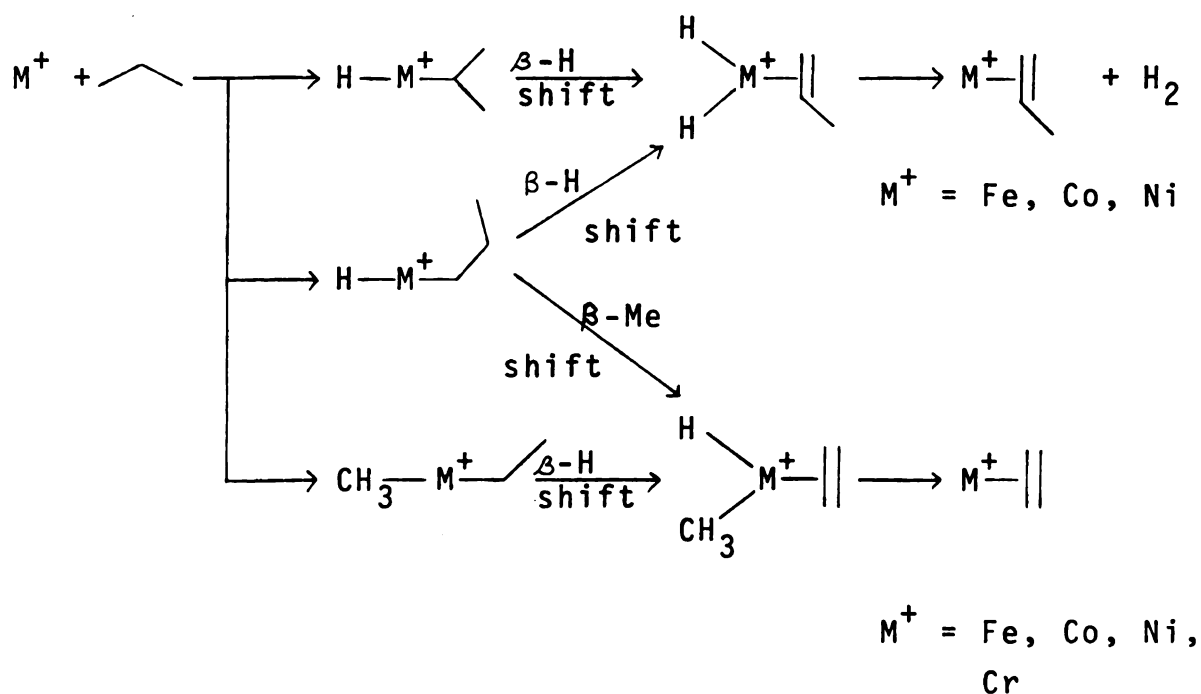
Ions formed as products of ion-molecule reactions in a mixture of Mo(CO)_6 and C_3H_8 are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
162	$\text{MoCO(C}_3\text{H}_6)^+$	MoCO^+ , Mo(CO)_2^+
190	$\text{Mo(CO)}_2\text{C}_3\text{H}_6^+$	Mo(CO)_2^+ , Mo(CO)_3^+
218	$\text{Mo(CO)}_3\text{C}_3\text{H}_6^+$	Mo(CO)_3^+

B. Discussion

Table 14 summarizes the reactions with propane for all five metal ions together with product distributions.

All the product ions seen can be explained in terms of the mechanism proposed by Beauchamp⁹⁴⁻⁹⁶.



Thus, Fe^+ , Co^+ and Ni^+ exhibit very similar reactivity with alkanes¹⁶⁴. It is of interest to note that Fe^+ , Ni^+ and Cr^+ have stronger preference to inserting into C-C bonds to eliminate smaller alkanes. Mo^+ , never induced any reactions from propane unless it has ligands attached. CO ligands on Mo^+ might affect the bonding abilities of other bonding orbitals. It is not surprising then since Mo^+ is a second row transition metal, which has larger d orbitals (60% size of 5s orbital) to make the bonds using the $4\text{d}z^2$ orbital, which in turn makes the second bond possible by use of other d orbitals (the promotion energy from 4d^n to $5\text{s}^1-4\text{d}^{n-1}$ to make a 5s orbital available for bonding¹²³ is about 72 kcal/mole). This contrasts with first row transition metals which bond almost exclusively using the 4s orbital. The 3d orbitals are only 30% the size of the 4s orbital and are tightly bound to the nucleus. (It is possible to mix 4s with 4p to make sp hybrid orbitals).

II. Reactions With Iodomethane (CH_3I)

A. Results

1. $\text{Fe}(\text{CO})_x^+$ reactions with CH_3I

Ions formed as products of ion-molecule reactions in a mixture of $\text{Fe}(\text{CO})_5$ and CH_3I are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
183	FeI^+	Fe^+
198	FeCH_3I^+	FeCO^+
226	$\text{FeCOCH}_3\text{I}^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$
254	$\text{Fe}(\text{CO})_2\text{CH}_3\text{I}^+$	$\text{Fe}(\text{CO})_2^+$, I^+ , $\text{Fe}(\text{CO})_3^+$, CH_3I^+ , $\text{Fe}(\text{CO})_4^+$
282	$\text{Fe}(\text{CO})_3\text{CH}_3\text{I}^+$	Fe^+ , $\text{Fe}(\text{CO})_3^+$, CH_3I^+ , $\text{Fe}(\text{CO})_4^+$

2. $\text{Co}(\text{CO})_x(\text{NO})_y^+$ reactions with CH_3I

Ions formed as products of ion-molecule reactions in a mixture of $\text{Co}(\text{CO})_3\text{NO}$ and CH_3I are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
186	CoI^+	CO^+
201	CoCH_3I^+	CoCO^+
229	$\text{CoCOCH}_3\text{I}^+$	CoCO^+ , $\text{Co}(\text{CO})_2^+$
231	$\text{CoNOCH}_3\text{I}^+$	CoCO^+ , CoCONO^+ , $\text{Co}(\text{CO})_2\text{NO}^+$
259	$\text{CoCONOCH}_3\text{I}^+$	CH_3I^+ , $\text{Co}(\text{CO})_2\text{NO}^+$, $\text{Co}(\text{CO})_3\text{NO}^+$
287	$\text{Co}(\text{CO})_2\text{NOCH}_3\text{I}^+$	$\text{Co}(\text{CO})_3\text{NO}^+$

3. $\text{Ni}(\text{CO})_x^+$ reactions with CH_3I

Ions formed as products of ion-molecule reactions in a mixture of $\text{Ni}(\text{CO})_4$ and CH_3I are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
185	NiI^+	Ni^+ , NiCO^+
200	NiCH_3I^+	Ni^+ , NiCO^+ , Ni(CO)_2^+
213	NiCOI^+	NiCO^+ , I^+
228	$\text{NiCOCH}_3\text{I}^+$	NiCO^+ , Ni(CO)_2^+ , Ni(CO)_3^+
256	$\text{Ni(CO)}_2\text{CH}_3\text{I}^+$	Ni(CO)_2^+ , I^+ , Ni(CO)_3^+ , Ni(CO)_4^+
284	$\text{Ni(CO)}_3\text{CH}_3\text{I}^+$	Ni(CO)_3^+ , Ni(CO)_4^+

4. Cr(CO)_x^+ reactions with CH_3I

Ions formed as products of ion-molecule reactions in a mixture of Cr(CO)_6 and CH_3I are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
179	CrI^+	Cr^+
194	CrCH_3I^+	CrCO^+ , Cr(CO)_2^+ , CH_3I^+

5. Mo(CO)_x^+ reactions with CH_3I

Ions formed as products of ion-molecule reactions in a mixture of Mo(CO)_6 and CH_3I are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
219	MoI^+	Mo^+
234	MoICH_3^+	$\text{Mo}^+, \text{MoCO}^+, \text{I}^+, \text{Mo(CO)}_3^+$

6. $\text{Al(CH}_3)_3^+$ reactions with CH_3I

Ions formed as products of ion-molecule reactions in a mixture of $\text{Al(CH}_3)_3$ and CH_3I are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
199	AlMe_3^{*+}	$\text{AlMe}_3^+, \text{CH}_3\text{I}^+$

* Me denotes a methyl group

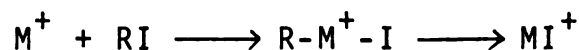
B. Discussion

Table 15 summarizes all the reactions with iodomethane for all metal ions in this work, together with their product distributions.

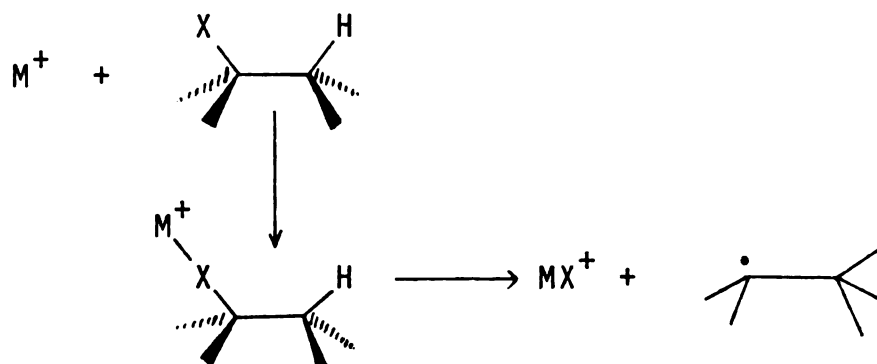
It appears that all metal ions insert into the polar bond (C-I in this case), followed by fragmentation to retain the iodine atom. Among them, Ni^+ seems to have the strongest interaction energy with CH_3I to induce more reactions. For example, Ni^+ is the only metal ion that produced MCOI^+ and MI^+ from NiCO^+ . Mo^+ follows almost the same reaction pattern as that of Cr^+ .

There are two possible mechanisms leading to the formation of Mi^+ :

(1)^{197,198}



(2)^{85,98,169-170}



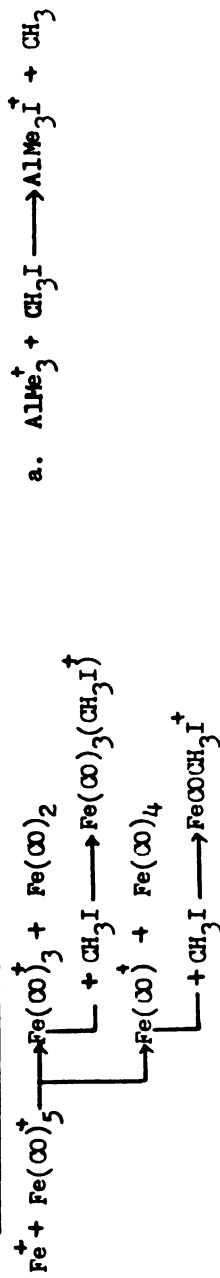
J. Allison and D.P. Ridge^{197,198} reported a number of first row transition metal ions reactions with alkyl halides and found the following results:

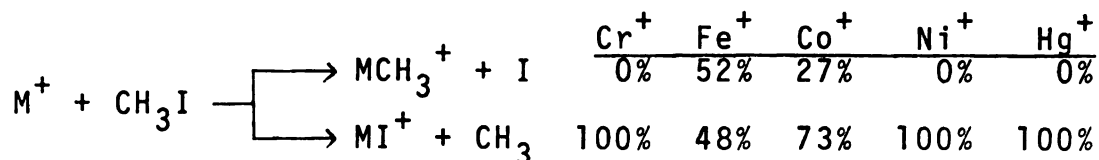
Table 15. Reactions With Iodomethane (CH₃I)

	Fe	Co	Ni	Cr	Mo	Al ^a
$\dot{M} + CH_3I \longrightarrow MI^+ + CH_3^-$	1.0	1.0	.93	1.0	.41	1.0
$\quad\quad\quad \downarrow$ $\quad\quad\quad MICH_3^\cdot$			.07		.59	

	Fe				Co			Ni				Cr		Mo		Al
	x=1	2	3	4	1	2	3	1	2	3	4	1	2	1	2	
$M(CO)_x^+ \rightarrow M(CO)_{x-1}(CH_3I)^+ + CO$	.98	.86	.65	.67	.94	1.0		.54	.89	.90	.24	.10		1.0		
$\rightarrow M(CO)_{x-2}(CH_3I)^+ + 2CO$				.33		1.0			.05	.06	.76		1.0			
$\rightarrow M(CO)_x(CH_3I)^+$					.06			.10	.06	.04						
$\rightarrow M(CO)_xI^+ + CH_3$								.06								
$\rightarrow M(CO)_{x-1}I^+ + CO + CH_3$								.30								
$M(CO)_xNO^+ \rightarrow M(CO)_{x-1}NO(CH_3I)^+ + CO$					1.0	.66	.77									
$\rightarrow M(CO)_{x-2}NO(CH_3I)^+ + 2CO$						.34	.23									

Successive reactions :





From the successive reactions study of labelled compounds, they proved that these transition metals do really insert into the carbon-halogen bond.

However, MCH_3^+ were not observed in this work as indicated in Table 15. The reasons being that the transition metal ions probably form a strong bond to iodine atom than $\cdot CH_3$ and due to the sensitivity of the instrument.

It is believed that nontransition metal ions follow mechanism (2) and first row transition metal ions follow the first mechanism. Obviously, the d orbitals in transition metals make them different from those nontransition metals.

III. Reactions with Isopropyl Chloride (C_3H_7Cl)

A. Results

$Fe(CO)_5$, $Co(CO)_3NO$ and $Ni(CO)_4$ reactions with isopropylchloride have been reported by Allison and Ridge⁸⁵. Thus they are not repeated here. $Cr(CO)_6$ and $Mo(CO)_6$ reactions with isopropylchloride are listed in the following.

1. $Cr(CO)_x^+$ reactions with isopropylchloride (C_3H_7Cl)

Ions formed as products of ion-molecule reactions in a mixture of $Cr(CO)_6$ and C_3H_7Cl are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
87	CrCl^+	Cr^+
88	CrHCl^+	Cr^+
94	CrC_3H_6^+	Cr^+ , CrCO^+
95	CrC_3H_7^+	Cr^+
122	$\text{CrCOC}_3\text{H}_6^+$	CrCO^+ , Cr(CO)_2^+
130	$\text{CrC}_3\text{H}_7\text{Cl}^+$	CrCO^+
158	$\text{CrCOC}_3\text{H}_7\text{Cl}^+$	Cr(CO)_2^+ , Cr(CO)_3^+
172	$\text{Cr(C}_3\text{H}_6\text{)(C}_3\text{H}_7\text{Cl)}^+$	CrCO^+ , Cr(CO)_2^+
186	$\text{Cr(CO)}_2\text{(C}_3\text{H}_7\text{Cl)}^+$	Cr(CO)_3^+ , Cr(CO)_4^+
208	$\text{Cr(C}_3\text{H}_7\text{Cl)}_2^+$	Cr(CO)_3^+ , Cr(CO)_3^+ $\text{CrCOC}_3\text{H}_7\text{Cl}^+$ $\text{Cr(C}_3\text{H}_6\text{)(C}_3\text{H}_7\text{Cl)}^+$

2. Mo(CO)_x^+ reactions with isopropylchloride
 $\text{(C}_3\text{H}_7\text{Cl)}$

Ions formed as products of ion-molecule reactions in a mixture of Mo(CO)_6 and $\text{C}_3\text{H}_7\text{Cl}$ are listed below, with their precursors as identified by double resonance.

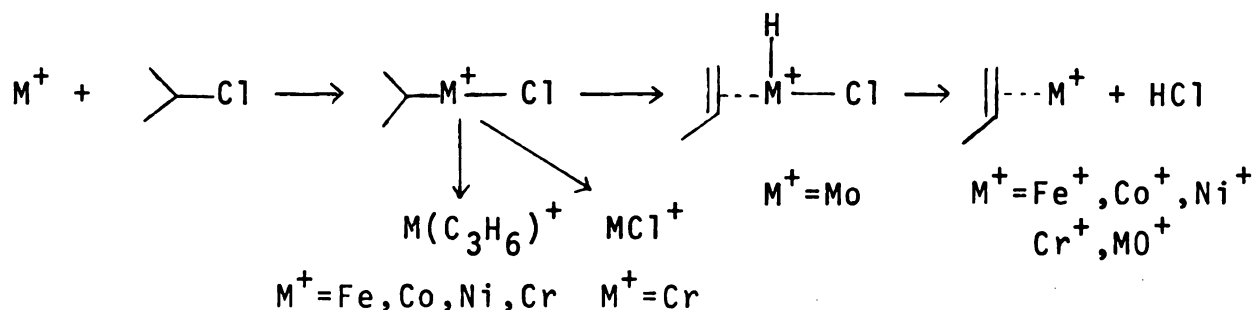
<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
134	$\text{Mo(C}_3\text{H}_6\text{)}^+$	Mo^+ , MoCO^+
162	$\text{MoCO(C}_3\text{H}_6\text{)}^+$	MoCO^+ , Mo(CO)_2^+
170	$\text{MoC}_3\text{H}_7\text{Cl}^+$	Mo^+ , MoCO^+ , Mo(CO)_2^+

B. Discussion

Table 16 summarizes the reactions with isopropylchloride for all five metal ions in this work together with product distributions. The formation of MC_3H_7^+ and MCl^+ is a good indication of insertion into the carbon-Cl polar bond for Fe^+ , Co^+ , Ni^+ and Cr^+ . The failure to observe MoC_3H_7^+ and MoI^+ may imply that direct fragmentation following inserting C-Cl bond to yield MC_3H_7^+ is a high energy pathway (radical loss).

From Tables 14, 15 and 16, it appears that Fe^+ , Co^+ and Ni^+ are capable of inserting into C-C and C-H bonds. Cr^+ prefers to insert into C-C bonds. Fe^+ , Co^+ , Ni^+ and Cr^+ form a stronger bond to iodide ($D(\text{M}^+-\text{I}) > 56.5$ kcal/mole) than Mo^+ .

Therefore, it seems that thermodynamics only can explain all the reactions presented to this point. The mechanism can be summarized below:



The formation of MC_3H_7^+ for Fe^+ , Co^+ , Ni^+ and Cr^+ implies that $D(\text{M}-\text{C}_3\text{H}_7)^+ > 82.03$ kcal/mole.

IV. Reactions with Cis-2-Pentene (C_5H_{10})A. Results1. $Fe(CO)_x^+$ reactions with cis-2- C_5H_{10}

Ions formed as products of ion-molecule reactions in a mixture of $Fe(CO)_5$ and C_5H_{10} are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
96	$Fe(C_3H_4)^+$	Fe^+ , $FeCO^+$
98	$Fe(C_3H_6)^+$	Fe^+ , $FeCO^+$
110	$Fe(C_4H_6)^+$	Fe^+ , $FeCO^+$
124	$Fe(C_5H_8)^+$	Fe^+ , $FeCO^+$
126	$Fe(C_5H_{10})^+$	$FeCO^+$, $Fe(CO)_2^+$
154	$FeCO(C_5H_{10})^+$	$FeCO^+$, $Fe(CO)_2^+$, $Fe(CO)_3^+$
182	$Fe(CO)_2(C_5H_{10})^+$ and $Fe(CO)_3C_3H_6^+$	$C_3H_6^+$, Fe , $Fe(CO)_3^+$ $Fe(CO)_4^+$
210	$Fe(CO)_3(C_5H_{10})^+$	$Fe(CO)_4^+$, $Fe(CO)_5^+$
238	$Fe(CO)_2(C_5H_{10})^+$	Fe^+ , $FeCO^+$, $Fe_2(CO)_4^+$

Note that m/e 182 is a mixture of $Fe(CO)_2(C_5H_{10})^+$ and $Fe(CO)_3(C_3H_6)^+$.

2. $Co(CO)_x(NO)_y^+$ reactions with cis-2- C_5H_{10}

Ions formed as products of ion-molecule reactions in a mixture of $Co(CO)_3NO$ and C_5H_{10} are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
99	$\text{Co}(\text{C}_3\text{H}_4)^+$	Co^+ , $\text{C}_5\text{H}_{10}^+$, CoCO^+
101	$\text{Co}(\text{C}_3\text{H}_6)^+$	Co^+ , CoCO^+
113	$\text{Co}(\text{C}_4\text{H}_6)^+$	Co^+ , CoCO^+
127	$\text{Co}(\text{C}_5\text{H}_8)^+$	Co^+ , CoCO^+
129	$\text{Co}(\text{C}_5\text{H}_{10})^+$	Co^+ , CoCO^+ , $\text{Co}(\text{CO})_2^+$
130	$\text{CoNOC}_3\text{H}_5^+$	C_3H_5^+ , CoCO^+ , $\text{Co}(\text{CO})_2^+$
156	$\text{CoCONOC}_3\text{H}_5^+$	C_3H_3^+ , C_3H_5^+
157	$\text{CoCOC}_5\text{H}_{10}^+$	CoCO^+ , $\text{Co}(\text{CO})_2^+$
158	$\text{CoCONOC}_3\text{H}_5^+$	C_3H_5^+ , $\text{Co}(\text{CO})_2\text{NO}^+$
159	$\text{CoNOC}_5\text{H}_{10}^+$	CoCONO^+ , $\text{Co}(\text{CO})_2\text{NO}^+$
187	$\text{CoCONOC}_5\text{H}_{10}^+$	C_3H_6^+ , $\text{C}_5\text{H}_{10}^+$, $\text{Co}(\text{CO})_2\text{NO}^+$, $\text{Co}(\text{CO})_3\text{NO}^+$
195	$\text{Co}(\text{C}_5\text{H}_8)_2^+$	CoCO^+ , $\text{Co}(\text{CO})_2^+$
199	$\text{Co}(\text{C}_5\text{H}_{10})_2^+$	CoCO^+ , $\text{Co}(\text{CO})_2^+$
215	$\text{Co}(\text{CO})_2\text{NOC}_5\text{H}_{10}^+$	$\text{C}_5\text{H}_{10}^+$
216	$\text{Co}_2\text{CO}(\text{C}_5\text{H}_{10})^+$	Co^+ , Co_2CONO^+
218	$\text{Co}_2\text{CONO}(\text{C}_3\text{H}_6)^+$	Co^+ , $\text{Co}(\text{C}_3\text{H}_6)^+$
229	$\text{CoNO}(\text{C}_5\text{H}_{10})_2^+$	Co^+ , $\text{C}_5\text{H}_{10}^+$, CoCO^+ , $\text{Co}(\text{CO})_2\text{NO}^+$, $\text{Co}(\text{CO})_3\text{NO}^+$
230	$\text{Co}(\text{C}_4\text{H}_6)(\text{CoCONO})^+$	Co^+ , CoCO^+ , $\text{Co}(\text{C}_4\text{H}_6)^+$
244	$\text{Co}_2\text{CONO}(\text{C}_5\text{H}_8)^+$	Co^+ , CoCO^+ , $\text{Co}_2(\text{CO})_2\text{NO}^+$
246	$\text{Co}_2\text{CONO}(\text{C}_5\text{H}_{10})^+$	Co^+ , CoCO^+

Note that C_3H_5^+ , C_3H_3^+ and C_3H_6^+ from organic fragmentations are reactive with neutral $\text{Co}(\text{CO})_3\text{NO}$ to form m/e 130,

156, 158 and m/e 187.

3. Ni(CO)_x^+ reactions with cis-2-pentene

Ions formed as products of ion-molecule reactions in a mixture of Ni(CO)_4 and C_5H_{10} are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
98	$\text{Ni(C}_3\text{H}_4)^+$	Ni^+
100	$\text{Ni(C}_3\text{H}_6)^+$	Ni^+ , NiCO^+
112	$\text{Ni(C}_4\text{H}_6)^+$	Ni^+ , NiCO^+
126	$\text{Ni(C}_5\text{H}_8)^+$	Ni^+ , NiCO^+
128	$\text{Ni(C}_5\text{H}_{10})^+$	Ni^+ , NiCO^+ , Ni(CO)_2^+
156	$\text{NiCO(C}_5\text{H}_{10})^+$	Ni(CO)_2^+ , Ni(CO)_3^+
170	Ni(CO)_4^+	$\text{C}_5\text{H}_{10}^+$
184	$\text{Ni(CO)}_2(\text{C}_5\text{H}_{10})^+$	$\text{C}_5\text{H}_{10}^+$, Ni(CO)_3 , Ni(CO)_4^+
198	$\text{Ni(C}_5\text{H}_{10})_2^+$	Ni(CO)_2^+ , Ni(CO)_3^+
212	$\text{Ni}_2\text{CO(C}_5\text{H}_8)^+$	Ni^+ , NiCO^+ , $\text{Ni}_2(\text{CO})_2^+$

Note that molecular ion of cis-2-pentene reacts by charge exchange with neutral Ni(CO)_4 to give m/e 170, Ni(CO)_4^+ .

4. Cr(CO)_x^+ reactions with cis-2-pentene

Ions formed as products of ion-molecule reactions in a mixture of Cr(CO)_6 and C_5H_{10} are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
120	$\text{Cr}(\text{C}_5\text{H}_8)^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$
122	$\text{Cr}(\text{C}_5\text{H}_{10})^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$
150	$\text{CrCO}(\text{C}_5\text{H}_{10})^+$	$\text{Cr}(\text{CO})_2^+$, $\text{Cr}(\text{CO})_3^+$

5. $\text{Mo}(\text{CO})_x^+$ reactions with cis-2-pentene

Ions formed as products of ion-molecule reactions in a mixture of $\text{Mo}(\text{CO})_6$ and C_5H_{10} are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
160	$\text{Mo}(\text{C}_5\text{H}_8)^+$	Mo^+ , MoCO^+
162	$\text{Mo}(\text{C}_5\text{H}_{10})^+$	Mo^+ , MoCO^+ , $\text{Mo}(\text{CO})_2^+$
188	$\text{MoCO}(\text{C}_5\text{H}_8)^+$	$\text{Mo}(\text{CO})_2^+$
190	$\text{MoCO}(\text{C}_5\text{H}_{10})^+$	$\text{Mo}(\text{CO})_2^+$
216	$\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_8)^+$	$\text{Mo}(\text{CO})_3^+$

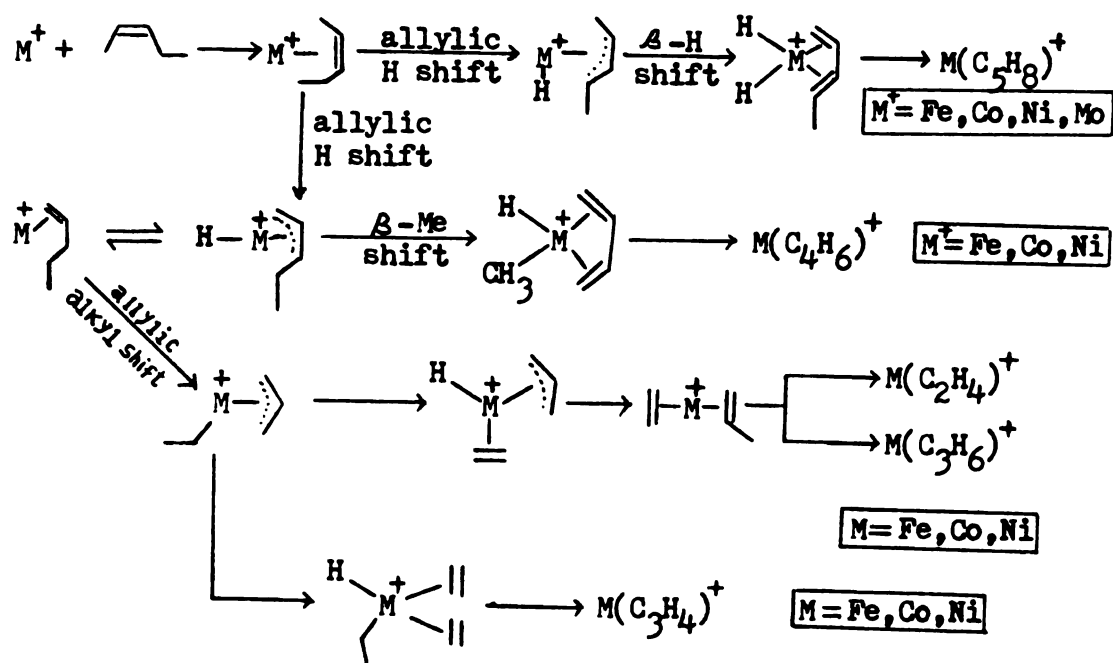
B. Discussion

Table 17 summarizes all the reactions of cis-2-pentene with metal and metal-containing ions in this work.

It is interesting to note that Cr^+ does not react with cis-2-pentene; Mo^+ only eliminates H_2 . When CO ligand(s) are attached, an elimination of H_2 is seen for both metal ions. It is also interesting to note that Cr^+ reacts with C_3H_8 to eliminate CH_4 . There thus appears to be a chain length effect¹⁷¹ or the double bond in alkenes prevents Cr^+ from inserting into C-C bonds. From Table 14 and 18, it can

be seen that Mo^+ does not insert into a C-C bond in either alkanes or alkenes.

The mechanism used to interpret the formation of all product ions can be summarized as follows (similar to those proposed by Beauchamp⁹⁷):



Note that these mechanisms also show a proposed pathway leading to the formation of $\text{M}(\text{C}_3\text{H}_6)^+$ and $\text{M}(\text{C}_3\text{H}_4)^+$, in which M^+ induces the isomerization of cis-2-pentene to 1-pentene as a first step. Similar isomerization steps have been previously reported^{91,97}.

V. Reactions with 1-Hexene (C_6H_{12})A. Results1. $Fe(CO)_x^+$ reactions with 1- C_6H_{12}

Ions formed as products of ion-molecule reactions in a mixture of $Fe(CO)_5$ and C_6H_{12} are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
84	$FeC_2H_4^+$	$C_2H_4^+$
98	$Fe(C_3H_6)^+$	Fe^+ , $FeCO^+$
110	$Fe(C_4H_6)^+$	Fe^+
140	$Fe(C_6H_{12})^+$	$FeCO^+$, $Fe(CO)_2^+$
153	$(C_3H_5)Fe(CO)_2^+$	$C_3H_5^+$
168	$FeCO(C_6H_{12})^+$	$Fe(CO)_3^+$
181	$Fe(CO)_3(C_3H_5)^+$	$C_3H_5^+$
196	$Fe(CO)_2(C_6H_{12})^+$	Fe^+ , $FeCO^+$, $Fe(CO)_4^+$
224	$Fe(CO)_3(C_6H_{12})^+$	Fe^+ , $FeCO^+$, $Fe(CO)_2^+$, $Fe(CO)_5^+$
250	$Fe_2(CO)_2(C_6H_{10})^+$	Fe^+ , $FeCO^+$
252	$Fe_2(CO)_2(C_6H_{12})^+$	Fe^+ , $FeCO^+$, $Fe(CO)_2^+$
266	$Fe_2(CO)_3(C_5H_{10})^+$	Fe^+ , $FeCO^+$
278	$Fe_2(CO)_3(C_6H_{10})^+$	$FeCO^+$
280	$Fe_2(CO)_3(C_6H_{12})^+$	$FeCO^+$, $Fe(CO)_2^+$, $Fe(CO)_3^+$

Note that $C_3H_5^+$ reacts with $Fe(CO)_5$ neutral to displace two or three CO's to form m/e 181 and 153 respectively. The formation of m/e 266 is hard to explain. Yet, this peak is reproducible.

2. $\text{Co(CO)}_x(\text{NO})_y^+$ reactions with 1-C₆H₁₂
(y=0,1)

Ions formed as products of ion-molecule reactions in a mixture of Co(CO)NO and C₆H₁₂ are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
101	$\text{Co(C}_3\text{H}_6)^+$	Co^+ , CoCO^+
143	$\text{Co(C}_6\text{H}_{12})^+$	Co^+ , CoCO^+ , Co(CO)_2^+
158	$\text{CoCONOC}_3\text{H}_5^+$	C_3H_5^+
172	$\text{CoCONOC}_4\text{H}_7^+$	C_4H_7^+
173	$\text{CoCONO(C}_4\text{H}_8)^+$ + $\text{CoNO(C}_6\text{H}_{12})^+$	C_4H_8^+ , $\text{C}_6\text{H}_{12}^+$, $\text{Co(CO)}_2\text{NO}^+$
201	$\text{CoCONO(C}_6\text{H}_{12})^+$	$\text{Co(CO)}_3\text{NO}^+$

Again, organic fragments C_3H_5^+ and C_4H_7^+ reacts with $\text{Co(CO)}_3\text{NO}$ neutral to form m/e 158 and 172 respectively. m/e 173 is the mixture of $\text{CoCONOC}_4\text{H}_8^+$, and $\text{CoNO(C}_6\text{H}_{12})^+$.

3. Ni(CO)_x^+ reactions with 1-C₆H₁₂

Ions formed as products of ion-molecule reactions in a mixture of Ni(CO)₄ and C₆H₁₂ are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
86	$\text{Ni}(\text{C}_2\text{H}_4)^+$	Ni^+
100	$\text{Ni}(\text{C}_3\text{H}_6)^+$	Ni^+ , NiCO^+
112	$\text{Ni}(\text{C}_4\text{H}_6)^+$	Ni^+ , NiCO
127	$\text{NiCO}(\text{C}_3\text{H}_5)^+$	C_3H_5^+
142	$\text{Ni}(\text{C}_6\text{H}_{12})^+$	Ni^+ , NiCO^+ , $\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{C}_3\text{H}_6)^+$
155	$\text{Ni}(\text{CO})_2(\text{C}_3\text{H}_5)^+$	C_3H_5^+
170	$\text{Ni}(\text{CO})_2(\text{C}_4\text{H}_8)^+$ + $\text{NiCO}(\text{C}_6\text{H}_{12})^+$	C_4H_8^+ , C_6H_{12} , $\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
198	$\text{Ni}(\text{CO})_3(\text{C}_4\text{H}_8)^+$ + $\text{Ni}(\text{CO})_2(\text{C}_6\text{H}_{12})^+$	C_4H_8^+ , $\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{CO})_4^+$

4. $\text{Cr}(\text{CO})_x^+$ reactions with 1- C_6H_{12}

Ions formed as products of ion-molecule reactions in a mixture of $\text{Cr}(\text{CO})_6$ and C_6H_{12} are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
134	$\text{Cr}(\text{C}_6\text{H}_{10})^+$	Cr^+ , CrCO^+ , $\text{Cr}(\text{CO})_2^+$
136	$\text{Cr}(\text{C}_6\text{H}_{12})^+$	Cr^+ , CrCO^+ , $\text{Cr}(\text{CO})_2^+$
164	$\text{CrCO}(\text{C}_6\text{H}_{12})^+$	$\text{Cr}(\text{CO})_2^+$, $\text{Cr}(\text{CO})_3^+$

5. $\text{Mo}(\text{CO})_x^+$ reactions with 1- C_6H_{12}

Ions formed as products of ion-molecule reactions in a mixture of $\text{Mo}(\text{CO})_6$ and C_6H_{12} are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
172	$\text{Mo}(\text{C}_6\text{H}_8)^+$	Mo^+ , MoCO^+ , $\text{Mo}(\text{CO})_2^+$
200	$\text{MoCO}(\text{C}_6\text{H}_8)^+$	$\text{Mo}(\text{CO})_2^+$, $\text{Mo}(\text{CO})_3^+$
204	$\text{MoCO}(\text{C}_6\text{H}_{12})^+$	$\text{Mo}(\text{CO})_2^+$, $\text{Mo}(\text{CO})_3^+$
228	$\text{Mo}(\text{CO})_2(\text{C}_6\text{H}_8)^+$	$\text{Mo}(\text{CO})_3^+$
232	$\text{Mo}(\text{CO})_2(\text{C}_6\text{H}_{12})^+$	$\text{Mo}(\text{CO})_3^+$

B. Discussion

Table 18 summarizes the reactions of 1-hexene with Fe^+ , Co^+ , Ni^+ , Cr^+ , and Mo^+ together with their product distributions.

Basically, the reactions of 1-hexene with these transition metal ion can be explained similarly to that proposed by Beauchamp⁹⁷, as follows:

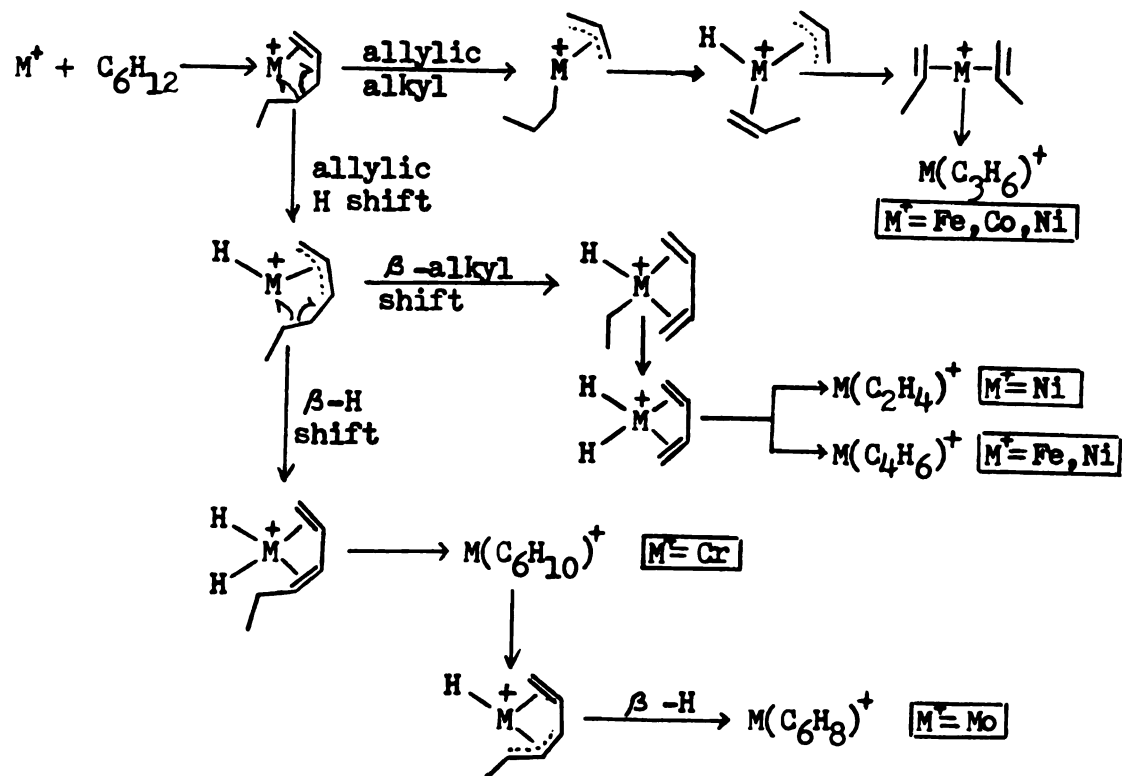
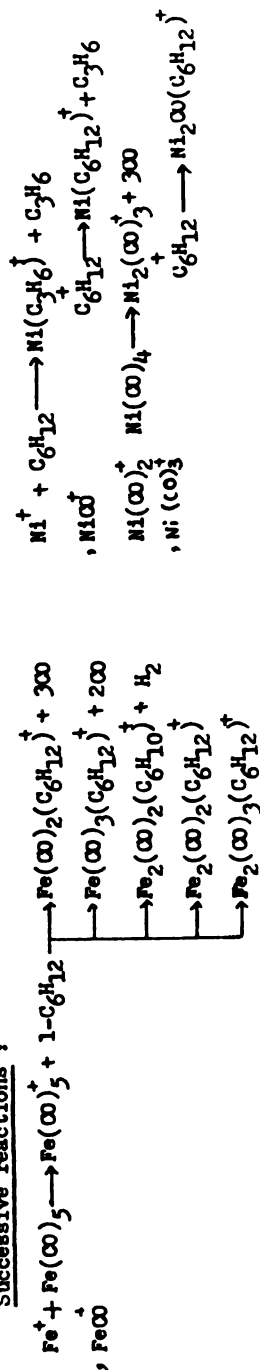


Table 18. Reactions With 1-Hexene (1-C₆H₁₂)

TABLE 4.9. REACTIONS WITH 1,2-HEXADIENE (1-6-12)

	Fe		Co		Ni				Cr			Mo		
	1	2	1	2	1	2	3	4	1	2	3	1	2	3
$M^+ + 1-C_6H_{12} \rightarrow M(C_2H_4)^+ + C_4H_8$														
$\rightarrow M(C_3H_6)^+ + C_3H_6$		.94				.84								
$\rightarrow M(C_4H_6)^+ + C_2H_6$		.06												
$\rightarrow M(C_6H_{12})$						.16					.91			
$\rightarrow M(C_6H_{10}) + H_2$											.09			
$\rightarrow M(C_6H_8) + 2H_2$													1.0	
$x =$														
$M(CO)_x^+ \rightarrow M(CO)_{x-1}(C_3H_6)^+ + C_3H_6^+ CO$		.65		.55		.45								
$\rightarrow M(CO)_{x-1}(C_4H_6)^+ + C_2H_6^+ CO$						.31								
$\rightarrow M(CO)_x(C_6H_{12})^+$								.10						
$\rightarrow M(CO)_{x-1}(C_6H_{12})^+ + CO$		.35		.45		.25	.13	.11	.15	.91	.17		.71	.62
$\rightarrow M(CO)_{x-2}(C_6H_{12})^+ + 2CO$														
$\rightarrow M(CO)_{x-1}(C_6H_{10})^+ + H_2 + CO$														
$\rightarrow M(CO)_{x-1}(C_6H_8)^+ + 2H_2 + CO$		1.0		1.0		.87	.79	.85	.09	.79	1.0			.10
$\rightarrow M(CO)_{x-2}(C_6H_8)^+ + 2H_2 + 2CO$														
$M(CO)_xNO^+ \rightarrow M(CO)_{x-2}NO(C_6H_{12})^+ + 2CO$														
						1.0	1.0					1.0	.13	.21
										.03			.15	.07

Successive reactions:



Note that Cr^+ and Mo^+ prefers to insert into C-H bonds to eliminate H_2 . Mo^+ can insert into C-H bonds to eliminate two hydrogen molecules. The intermediates having C_3H_5^+ or four π electrons distributed on three carbons are reasonable, because they are good π -donor ligands and exist as the stable fragments in the mass spectrometers^{87,168}.

VI. Reactions with 2-pentanone ($2\text{-C}_5\text{H}_{10}\text{O}$)

A. Results

1. $\text{Fe}(\text{CO})_x^+$ reactions with $2\text{-C}_5\text{H}_{10}\text{O}$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Fe}(\text{CO})_5$ and $\text{C}_5\text{H}_{10}\text{O}$ are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
84	FeC_2H_4^+	C_2H_4^+
114	$\text{Fe}(\text{C}_3\text{H}_6\text{O})^+$	Fe^+ , FeCO^+
140	$\text{Fe}(\text{C}_5\text{H}_8\text{O})^+$	Fe^+ , FeCO^+
142	$\text{Fe}(\text{C}_5\text{H}_{10}\text{O})^+$	Fe^+ , FeCO^+ , $\text{Fe}(\text{CO})_2^+$
170	$\text{FeCO}(\text{C}_5\text{H}_{10}\text{O})^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$
181	$\text{Fe}(\text{CO})_3\text{C}_3\text{H}_5^+$	C_3H_5^+ , C_3H_7^+
183	$\text{Fe}(\text{CO})_3\text{C}_3\text{H}_7^+$	C_3H_7^+
197	$\text{Fe}(\text{CO})_5\text{H}^+$	C_3H_7^+
198	$\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_{10}\text{O})^+$	$\text{Fe}(\text{CO})_3^+$, $\text{Fe}(\text{CO})_4^+$
211	$\text{Fe}(\text{CO})_4\text{C}_3\text{H}_7^+$	C_3H_7^+ , $\text{C}_5\text{H}_{10}\text{O}^+$
226	$\text{Fe}(\text{CO})_3(\text{C}_5\text{H}_{10}\text{O})^+$	$\text{Fe}(\text{CO})_4^+$, $\text{Fe}(\text{CO})_5^+$
228	$\text{Fe}(\text{C}_5\text{H}_{10}\text{O})_2^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$,

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
		$\text{FeCO}(\text{C}_5\text{H}_{10}\text{O})^+$,
		$\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_{10}\text{O})^+$

Note that C_3H_5^+ and C_3H_7^+ react with $\text{Fe}(\text{CO})_5$ neutral to yield m/e 181 and 183 and 211 respectively. Also, C_3H_7^+ can protonate $\text{Fe}(\text{CO})_5$ to produce $\text{Fe}(\text{CO})_5\text{H}^+$.

2. $\text{Co}(\text{CO})_x(\text{NO})_y^+$ reactions with $2\text{-C}_5\text{H}_{10}\text{O}$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Co}(\text{CO})_3\text{NO}$ and $\text{C}_5\text{H}_{10}\text{O}$ are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
117	$\text{Co}(\text{C}_3\text{H}_6\text{O})^+$	Co^+ , CoCO^+
143	$\text{Co}(\text{C}_5\text{H}_8\text{O})^+$	Co^+ , CoCO^+
145	$\text{Co}(\text{C}_5\text{H}_{10}\text{O})^+$	Co^+ , CoCO^+ , $\text{Co}(\text{CO})_2^+$
158	$\text{CoCONOC}_3\text{H}_5^+$	C_3H_5^+
173	$\text{CoCO}(\text{C}_5\text{H}_{10}\text{O})^+$	CoCO^+ , $\text{Co}(\text{CO})_2^+$
175	$\text{CoNO}(\text{C}_5\text{H}_{10}\text{O})^+$	CoCONO^+ , $\text{Co}(\text{CO})_2\text{NO}^+$
203	$\text{CoCONO}(\text{C}_5\text{H}_{10}\text{O})^+$	$\text{C}_5\text{H}_{10}\text{O}^+$, CoCONO^+ , $\text{Co}(\text{CO})_2\text{NO}^+$, $\text{Co}(\text{CO})_3\text{NO}^+$
216	$\text{CoNO}(\text{C}_5\text{H}_{10})(\text{C}_3\text{H}_5)^+$	C_3H_5^+
128	$\text{CoNO}(\text{C}_5\text{H}_{10}\text{O})(\text{C}_3\text{H}_7)^+$	C_3H_7^+
229	$\text{Co}(\text{C}_5\text{H}_8\text{O})(\text{C}_5\text{H}_{10}\text{O})^+$	Co^+ , CoCO^+ , $\text{Co}(\text{C}_5\text{H}_8\text{O})^+$
231	$\text{Co}(\text{C}_5\text{H}_{10}\text{O})_2^+$	Co^+ , CoCO^+ , $\text{Co}(\text{CO})_2^+$, CoCONO^+ , $\text{Co}(\text{CO})_2\text{NO}^+$, $\text{Co}(\text{CO})_3\text{NO}^+$, $\text{C}_5\text{H}_{10}\text{O}^+$

Again, C_3H_5^+ reacts with $\text{Co}(\text{CO})_3\text{NO}$ neutral to produce m/e 158 and m/e 216. C_3H_7^+ reacts with $\text{Co}(\text{CO})_3\text{NO}$ to produce m/e 218.

3. $\text{Ni}(\text{CO})_x^+$ reactions with 2- $\text{C}_5\text{H}_{10}\text{O}$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Ni}(\text{CO})_4$ and $\text{C}_5\text{H}_{10}\text{O}$ are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
100	$\text{Ni}(\text{C}_3\text{H}_6)^+$	Ni^+ , NiCO^+
102	$\text{Ni}(\text{C}_2\text{H}_4\text{O})^+$	Ni^+ , NiCO^+
116	$\text{Ni}(\text{C}_3\text{H}_6\text{O})^+$	Ni^+ , NiCO^+
144	$\text{Ni}(\text{C}_5\text{H}_{10}\text{O})^+$	Ni^+ , NiCO^+ , $\text{Ni}(\text{CO})_2^+$
155	$\text{Ni}(\text{CO})_2\text{C}_3\text{H}_5^+$	C_3H_5^+
157	$\text{Ni}(\text{CO})_2\text{C}_3\text{H}_7^+$	C_3H_7^+
172	$\text{NiCO}(\text{C}_5\text{H}_{10}\text{O})^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
230	$\text{Ni}_2\text{CO}(\text{C}_5\text{H}_{10}\text{O})^+$	NiCO^+ , $\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{C}_5\text{H}_{10}\text{O})^+$, $\text{Ni}(\text{CO})_4^+$, $\text{NiCO}(\text{C}_5\text{H}_{10}\text{O})^+$

Similarly, C_3H_5^+ and C_3H_7^+ react with $\text{Ni}(\text{CO})_4$ neutral to give m/e 155 and m/e 157 respectively to displace 2 CO's.

4. $\text{Cr}(\text{CO})_x^+$ reactions with 2- $\text{C}_5\text{H}_{10}\text{O}$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Cr}(\text{CO})_6$ and $\text{C}_5\text{H}_{10}\text{O}$ are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
138	$\text{Cr}(\text{C}_5\text{H}_{10}\text{O})^+$	Cr^+ , CrCO^+
166	$\text{CrCO}(\text{C}_5\text{H}_{10}\text{O})^+$	$\text{Cr}(\text{CO})_2^+$, $\text{Cr}(\text{CO})_3^+$
224	$\text{Cr}(\text{C}_5\text{H}_{10}\text{O})_2^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$, $\text{Cr}(\text{CO})_3^+$

5. $\text{Mo}(\text{CO})_x^+$ reactions with 2- $\text{C}_5\text{H}_{10}\text{O}$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Mo}(\text{CO})_6$ and $\text{C}_5\text{H}_{10}\text{O}$ are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
174	$\text{Mo}(\text{C}_5\text{H}_6\text{O})^+$	Mo^+
176	$\text{Mo}(\text{C}_5\text{H}_8\text{O})^+$	Mo^+ , MoCO^+
178	$\text{Mo}(\text{C}_5\text{H}_{10}\text{O})^+$	Mo^+ , MoCO^+ , $\text{Mo}(\text{CO})_2^+$
204	$\text{MoCO}(\text{C}_5\text{H}_8\text{O})^+$	$\text{Mo}(\text{CO})_2^+$, $\text{Mo}(\text{CO})_3^+$
232	$\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_8\text{O})^+$	$\text{Mo}(\text{CO})_3^+$, $\text{Mo}(\text{CO})_4^+$

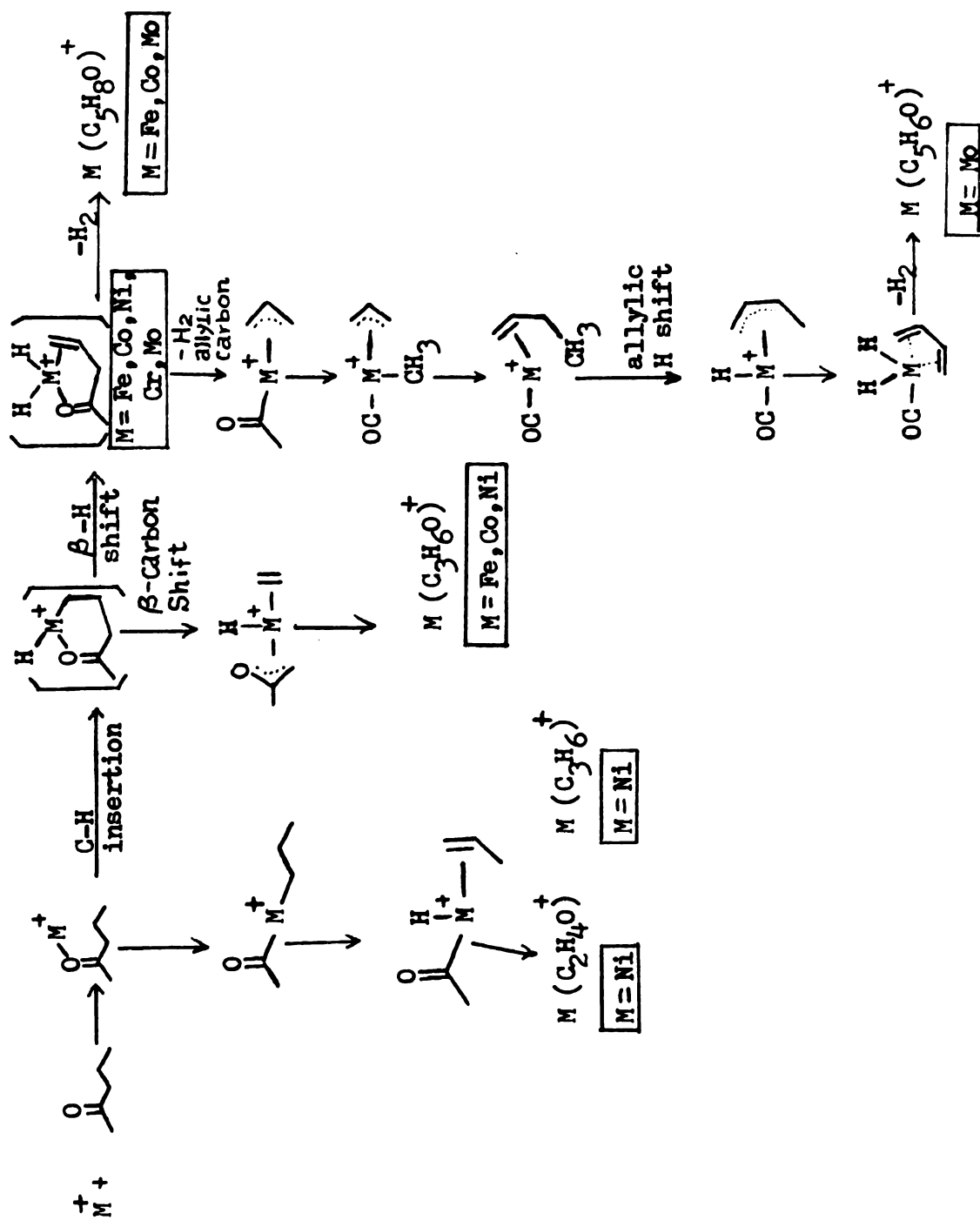
B. Discussion

Table 19 summarizes the Fe^+ , Co^+ , Ni^+ , Cr^+ and Mo^+ reactions with 2-pentanone, together with their product distributions.

The formation of all reaction products can be explained very similarly to the mechanism proposed by Freiser⁸⁷ et. al. as shown in Scheme XXIX.

Note that Fe^+ , Co^+ , Ni^+ , Cr^+ and Mo^+ can form stable addition products, $\text{M}(\text{C}_5\text{H}_{10}\text{O})^+$. Ni^+ and Cr^+ failed to eliminate H_2 . However, Mo^+ has extra energy to eliminate one

Scheme XXIX



more H_2 to form $\text{Mo}(\text{C}_5\text{H}_6\text{O})^+$, implying that Mo^+ has the strongest tendency to insert into a C-H bond. It is of interest also to note that Ni^+ is the only metal which can insert into a carbonyl-carbon bond, producing $\text{Ni}(\text{C}_2\text{H}_4\text{O})^+$ and $\text{Ni}(\text{C}_3\text{H}_6)^+$. Freiser⁸⁷ also reported to see FeCO^+ and $\text{Fe}(\text{C}_2\text{H}_4)^+$ in a trace amount (< 1%) in the reaction of Fe^+ with 2-pentanone, which is not observed in our experiment. Another trace amount (6%) of the product ion, $\text{Fe}(\text{C}_4\text{H}_8)^+$ reported by Freiser is not observed in our experiment.

VII. Reactions with sec-Butylamine (s-BUNH_2 , $\text{C}_4\text{H}_{11}\text{N}$)

A. Results

1. $\text{Fe}(\text{CO})_x^+$ reactions with sec-butylamine (s-BUNH_2 , $\text{C}_4\text{H}_{11}\text{N}$)

Ions formed as products of ion-molecule reactions in a mixture of $\text{Fe}(\text{CO})_5$ and sBUNH_2 are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
87	$\text{Fe}(\text{CH}_3\text{NH}_2)^+$	Fe^+ , FeCO^+
98	$\text{Fe}(\text{C}_3\text{H}_6)^+$	FeCO^+
110	$\text{Fe}(\text{C}_4\text{H}_6)^+$	Fe^+
113	$\text{Fe}(\text{C}_3\text{H}_7\text{N})^+$	Fe^+ , FeCO^+
114	$\text{Fe}(\text{C}_3\text{H}_6\text{NH}_2)^+$	Fe^+ , FeCO^+
125	$\text{Fe}(\text{C}_4\text{H}_7\text{N})^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$
127	$\text{Fe}(\text{C}_4\text{H}_7\text{NH}_2)^+$	Fe^+ , FeCO^+
128	$\text{FeCO}(\text{C}_2\text{H}_6\text{N})^+$	FeCO^+

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
129	$\text{Fe}(\text{C}_4\text{H}_9\text{NH}_2)^+$	FeCO^+ , $\text{Fe}(\text{CO})_2^+$
157	$\text{FeCO}(\text{C}_4\text{H}_9\text{NH}_2)^+$	$\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$, $\text{Fe}(\text{CO})_4^+$
185	$\text{Fe}(\text{CO})_2(\text{C}_4\text{H}_9\text{NH}_2)^+$	$\text{Fe}(\text{CO})_4^+$, $\text{Fe}(\text{CO})_5^+$
202	$\text{Fe}(\text{C}_4\text{H}_9\text{NH}_2)_2^+$	FeCO^+ , $\text{Fe}(\text{CO})_2^+$, $\text{Fe}(\text{CO})_3^+$, $\text{Fe}(\text{CO})_4^+$

2. $\text{Co}(\text{CO})_x(\text{NO})_y^+$ reactions with sec-butylamine
sBUNH₂, C₄H₁₁N

Ions formed as products of ion-molecule reactions in a mixture of $\text{Co}(\text{CO})_3\text{NO}$ and sBUNH₂ are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
90	$\text{Co}(\text{CH}_3\text{NH}_2)^+$	Co^+
100	$\text{Co}(\text{C}_3\text{H}_5)^+$	CoCO^+
102	$\text{Co}(\text{C}_2\text{H}_5\text{NH}_2)^+$	Co^+ , CoCO^+
104	$\text{Co}(\text{C}_2\text{H}_5\text{NH}_2)^+$	Co^+ , CoCO^+
113	$\text{Co}(\text{C}_4\text{H}_6)^+$	Co^+
116	$\text{Co}(\text{C}_3\text{H}_7\text{N})^+$	Co^+ , CoCO^+
128	$\text{Co}(\text{C}_4\text{H}_7\text{N})^+$	Co^+
130	$\text{Co}(\text{C}_4\text{H}_7\text{NH}_2)^+$	Co^+ , CoCO^+
132	$\text{Co}(\text{C}_4\text{H}_9\text{NH}_2)^+$	Co^+ , CoCO^+ , $\text{Co}(\text{CO})_2^+$
160	$\text{CoCO}(\text{C}_4\text{H}_9\text{NH}_2)^+$	CoCO^+ , $\text{Co}(\text{CO})_2^+$
162	$\text{CoNO}(\text{C}_4\text{H}_9\text{NH}_2)^+$	CoCONO^+ , $\text{Co}(\text{CO})_2\text{NO}^+$ $\text{Co}(\text{CO})_3\text{NO}^+$

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
190	$\text{CoCONO}(\text{C}_4\text{H}_9\text{NH}_2)^+$	$\text{Co}(\text{CO})_3\text{NO}^+$
205	$\text{Co}(\text{C}_4\text{H}_9\text{NH}_2)_2^+$	Co^+ , CoCO^+ , $\text{Co}(\text{CO})_2^+$
221	$\text{Co}_2\text{NO}(\text{C}_4\text{H}_9\text{NH}_2)^+$	Co^+
249	$\text{Co}_2\text{CONO}(\text{C}_4\text{H}_9\text{NH}_2)^+$	CoCO^+

3. $\text{Ni}(\text{CO})_x^+$ reactions with sec-butylamine
 $(\text{sBuNH}_2, \text{C}_4\text{H}_{11}\text{N})$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Ni}(\text{CO})_4$ and sBuNH_2 are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
72	$\text{C}_4\text{H}_{10}\text{N}^+$	Ni^+ , NiCO^+
89	$\text{Ni}(\text{CH}_3\text{NH}_2)^+$	NiCO
103	$\text{Ni}(\text{C}_2\text{NH}_2)^+$	Ni^+ , NiCO^+ , $\text{Ni}(\text{CO})_2^+$
115	$\text{Ni}(\text{C}_3\text{H}_5\text{NH}_2)^+$	Ni^+ , NiCO^+
117	$\text{NiCO}(\text{CH}_3\text{NH}_2)^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
127	$\text{Ni}(\text{C}_4\text{H}_7\text{N})^+$	Ni^+
128	$\text{NiCO}(\text{CH}_3\text{CHNH}_2)^+$	$\text{CH}_3\text{CHNH}_2^+$
129	$\text{Ni}(\text{C}_4\text{H}_7\text{NH}_2)^+$	Ni^+
131	$\text{Ni}(\text{C}_4\text{H}_9\text{NH}_2)^+$	NiCO^+ , $\text{Ni}(\text{C}_2\text{H}_5\text{NH}_2)^+$, $\text{Ni}(\text{CO})_2^+$
132	$\text{NiCO}(\text{C}_4\text{H}_6)^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$
145	$\text{Ni}(\text{CO})_2(\text{CH}_3\text{NH}_2)^+$	$\text{Ni}(\text{CO})_4^+$
159	$\text{NiCO}(\text{C}_4\text{H}_9\text{NH}_2)^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{CO})_4^+$

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
204	$\text{Ni}(\text{C}_4\text{H}_9\text{NH}_2)_2^+$	$\text{Ni}(\text{CO})_2^+$, $\text{Ni}(\text{CO})_3^+$, $\text{Ni}(\text{CO})_4^+$, $\text{Ni}(\text{C}_4\text{H}_9\text{NH}_2)^+$, $\text{NiCO}(\text{C}_4\text{H}_9\text{NH}_2)^+$
215	$\text{Ni}_2\text{CO}(\text{C}_4\text{H}_7\text{NH}_2)^+$	Ni^+ , NiCO^+ , $\text{Ni}_2(\text{CO})_2^+$

4. $\text{Cr}(\text{CO})_x^+$ reactions with sec-butylamine
 $(\text{sBUNH}_2, \text{C}_4\text{H}_{11}\text{N})$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Cr}(\text{CO})_6$ and sBUNH_2 are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
112	$\text{CrCOCH}_3\text{NH}_3^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$
123	$\text{Cr}(\text{C}_4\text{H}_7\text{NH}_2)^+$	Cr^+ , CrCO^+ , $\text{Cr}(\text{CO})_2^+$
125	$\text{Cr}(\text{C}_4\text{H}_9\text{NH}_2)^+$	Cr^+ , CrCO^+ , $\text{Cr}(\text{CO})_2^+$
153	$\text{CrCO}(\text{C}_4\text{H}_9\text{NH}_2)^+$	$\text{Cr}(\text{CO})_2^+$, $\text{Cr}(\text{CO})_3^+$, $\text{Cr}(\text{CO})_4^+$
198	$\text{Cr}(\text{C}_4\text{H}_9\text{NH}_2)_2^+$	CrCO^+ , $\text{Cr}(\text{CO})_2^+$, $\text{Cr}(\text{C}_4\text{H}_9\text{NH}_2)^+$, $\text{Cr}(\text{CO})_3^+$, $\text{CrCo}(\text{C}_4\text{H}_9\text{NH}_2)^+$

5. $\text{Mo}(\text{CO})_x^+$ reactions with sec-butylamine
 $(\text{sBUNH}_2, \text{C}_4\text{H}_{11}\text{N})$

Ions formed as products of ion-molecule reactions in a mixture of $\text{Mo}(\text{CO})_6$ and sBUNH_2 are listed below, with their precursors as identified by double resonance.

<u>m/e</u>	<u>stoichiometry</u>	<u>precursor(s)</u>
161	$\text{Mo}(\text{C}_4\text{H}_7\text{N})^+$	Mo^+ , MoCO^+
163	$\text{Mo}(\text{C}_4\text{H}_7\text{NH}_2)^+$	Mo^+ , MoCO^+
165	$\text{Mo}(\text{C}_4\text{H}_9\text{NH}_2)^+$	MoCO^+ , $\text{Mo}(\text{CO})_2^+$
191	$\text{MoCO}(\text{C}_4\text{H}_7\text{NH}_2)^+$	$\text{Mo}(\text{CO})_2^+$, $\text{Mo}(\text{CO})_3^+$
217	$\text{Mo}(\text{CO})_2(\text{C}_4\text{H}_7\text{N})^+$	$\text{Mo}(\text{CO})_3^+$
219	$\text{Mo}(\text{CO})_2(\text{C}_4\text{H}_7\text{NH}_2)^+$	$\text{Mo}(\text{CO})_3^+$

6. $\text{W}(\text{CO})_x^+$ reactions with sec-butylamine
(sBUNH₂, C₄H₁₁N)

$\text{W}(\text{CO})_x^+$ reactions with sec-butylamine were also studied by use of the CEC 21-110 B double focusing mass spectrometer without precursors identification. The reaction products are listed below:

<u>m/e</u>	<u>stoichiometry</u>
225	$\text{WC}(\text{CH}_3\text{NH}_2)^+$
237	$\text{W}(\text{C}_3\text{H}_5\text{N})^+$
249	$\text{WC}(\text{C}_3\text{H}_5\text{N})^+$
251	$\text{W}(\text{C}_4\text{H}_7\text{N})^+$
253	$\text{W}(\text{C}_4\text{H}_7\text{NH}_2)^+$
279	$\text{WCO}(\text{C}_4\text{H}_7\text{N})^+$
307	$\text{W}(\text{CO})_2(\text{C}_4\text{H}_7\text{N})^+$
309	$\text{W}(\text{CO})_2(\text{C}_4\text{H}_7\text{NH}_2)^+$
337	$\text{W}(\text{CO})_3(\text{C}_4\text{H}_7\text{NH}_2)^+$
343	$\text{W}(\text{CO})_3(\text{C}_4\text{H}_9\text{NH}_2)^+$

B. Discussion

Table 20 summarizes the Fe^+ , Co^+ , Ni^+ , Cr^+ and Mo^+ reactions with sec-butylamine and also their product distributions.

Scheme XXX shows a proposed mechanism leading to the formation of reaction products.

It is of interest to note that Ni^+ undergoes a hydride abstraction from sec-butylamine to yield $\text{C}_4\text{H}_{10}\text{N}^+$ and that Fe^+ forms a high energy product, $\text{Fe}(\text{C}_3\text{H}_8\text{N})^+$ by losing a methyl group after inserting into the C-C bond of sec-butylamine.

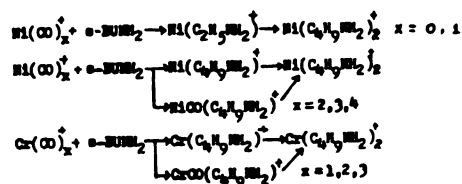
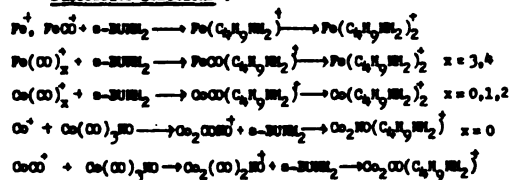
Table 20 also shows a trend that Fe^+ , Co^+ and Ni^+ exhibit much richer chemistries in their reactions with sec-butylamine. However, Cr^+ , Mo^+ , and W^+ are mostly inducing hydrogen molecule(s) elimination. Note that WC^+ is a reactive species, since it produces $\text{WC}(\text{CH}_3\text{NH}_2)^+$. Also, W^+ is the only species which can eliminate both CH_4 and H_2 to product $\text{W}(\text{C}_3\text{H}_5\text{N})^+$. In Scheme XXX, a process pathway leading to the formation of $\text{M}(\text{CH}_3\text{NH}_2)^+$ is also shown. Note that this process needs an isomerization of sec-butylamine to isobutylamine. Similar isomerization steps have been previously reported^{91,97}.

Also shown in Scheme XXX are pathways leading to the formation of $\text{Fe}(\text{C}_3\text{H}_6)^+$, $\text{Fe}(\text{C}_4\text{H}_7\text{N})^+$, $\text{Co}(\text{C}_3\text{H}_5)^+$, $\text{Ni}(\text{CH}_3\text{NH}_2)^+$ with a concurrent loss of the CO ligand.

Table 20. Reactions With Sec-Butylamine (S-BU₂)

		Fe				Co				Ni				Cr				Mn			
		1	2	3	4	1	2	3		1	2	3	4	1	2	3		1	2	3	
$\text{H}^+ + \text{S-BU}_2 \rightarrow$	$\text{H}^+ + \text{C}_6\text{H}_5\text{NO}_2^+$																				
	$\rightarrow \text{H}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{C}_6\text{H}_5$																				
	$\rightarrow \text{H}(\text{C}_2\text{H}_5\text{NO}_2)^+ + \text{C}_2\text{H}_5 + \text{H}_2$																				
	$\rightarrow \text{H}(\text{C}_2\text{H}_5\text{NO}_2)^+ + \text{C}_2\text{H}_5$																				
	$\rightarrow \text{H}(\text{C}_6\text{H}_6)^+ + \text{H}_2 + \text{H}_2$																				
	$\rightarrow \text{H}(\text{C}_3\text{H}_7\text{NO}_2)^+ + \text{CH}_3$																				
	$\rightarrow \text{H}(\text{C}_3\text{H}_7\text{NO}_2)^+ + \text{CH}_3$																				
	$\rightarrow \text{H}(\text{C}_6\text{H}_5\text{NO}_2)^+ + 2\text{H}_2$																				.20
	$\rightarrow \text{H}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{H}_2$																				.80
	$\rightarrow \text{H}(\text{C}_6\text{H}_5\text{NO}_2)^+$																				
$x =$		1	2	3	4	1	2	3		1	2	3	4	1	2	3		1	2	3	
$\text{H}(\text{CO})_x^+$	$\rightarrow \text{H}(\text{CO})_{x-1}^+ + \text{C}_6\text{H}_5\text{NO}_2 + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{C}_6\text{H}_5 + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-2}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{C}_6\text{H}_5 + 2\text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_x(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{C}_6\text{H}_5$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{C}_6\text{H}_5 + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}(\text{C}_2\text{H}_5\text{NO}_2)^+ + \text{C}_2\text{H}_5 + \text{H}_2 + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_x(\text{C}_2\text{H}_5\text{NO}_2)^+ + \text{C}_2\text{H}_5$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}(\text{C}_2\text{H}_5\text{NO}_2)^+ + \text{C}_2\text{H}_5 + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-2}(\text{C}_2\text{H}_5\text{NO}_2)^+ + \text{C}_2\text{H}_5 + 2\text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}(\text{C}_2\text{H}_5\text{NO}_2)^+ + \text{CH}_3\text{NO}_2 + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}(\text{C}_2\text{H}_5\text{NO}_2)^+ + \text{CH}_3\text{NO}_2 + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}(\text{C}_6\text{H}_6)^+ + \text{H}_2 + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-2}(\text{C}_6\text{H}_6)^+ + \text{H}_2 + 2\text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{CH}_3 + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{CH}_3 + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{H}_2 + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-2}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{H}_2 + 2\text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}(\text{C}_6\text{H}_5\text{NO}_2)^+ + 2\text{H}_2 + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-2}(\text{C}_6\text{H}_5\text{NO}_2)^+ + 2\text{H}_2 + 2\text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-3}(\text{C}_6\text{H}_5\text{NO}_2)^+ + 2\text{H}_2 + 3\text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_x(\text{C}_6\text{H}_5\text{NO}_2)^+$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-2}(\text{C}_6\text{H}_5\text{NO}_2)^+ + 2\text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-3}(\text{C}_6\text{H}_5\text{NO}_2)^+ + 3\text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}\text{NO}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-2}\text{NO}(\text{C}_6\text{H}_5\text{NO}_2)^+ + 2\text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-3}\text{NO}(\text{C}_6\text{H}_5\text{NO}_2)^+ + 3\text{CO}$																				
$x =$		1	2	3	4	1	2	3		1	2	3	4	1	2	3		1	2	3	
$\text{H}(\text{CO})_x\text{NO}^+$	$\rightarrow \text{H}(\text{CO})_{x-1}\text{NO}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-2}\text{NO}(\text{C}_6\text{H}_5\text{NO}_2)^+ + 2\text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-3}\text{NO}(\text{C}_6\text{H}_5\text{NO}_2)^+ + 3\text{CO}$																				
	$\rightarrow \text{H}(\text{CO})_{x-1}\text{NO}(\text{C}_6\text{H}_5\text{NO}_2)^+ + \text{CO}$																				

Successive reactions:



There are some new reaction products which are not seen in metals alone. The formation of $\text{CrCO}(\text{CH}_3\text{NH}_3)^+$ can be explained similarly to the formation of $\text{M}(\text{CH}_3\text{NH}_2)^+$ in Scheme XXX except that one more β -H shifts from the left side to give $\text{CrCO}(\text{C}_3\text{H}_5)(\text{CH}_3\text{NH}_3)^+$ followed by a simple fragmentation. The formation of $\text{FeCO}(\text{C}_2\text{H}_6\text{N})^+$ can be explained by the FeCO^+ insertion between skeletal atoms C2 and C3 with CO acting as a spectator (because CO is retained on Fe^+). Note that the loss of $\text{C}_3\text{H}_5\cdot$ radical which is also seen in CID spectra of Co^+ reactions with alkanes¹⁶⁶ is a high energy process.

VIII. Conclusions

Based on our original goals, we have the following results from this work:

1. All transition metal ions in this work insert into a C-I bond.
2. All transition metal ions in this work induce a β -H shift.
3. It is hard to tell if 5 or 6 membered rings are preferred in the intermediates. It appears that 6-membered rings are the preferred intermediates in the reactions with 2-pentanone.

Apparently, one cannot yet explicitly explain the differences of metal ions in terms of the controlling factors which were assumed in the beginning of this section. However, from this study, it seems that thermodynamics only

dominates the reactions disregarding geometrical considerations.

From this study, we do see a certain pattern of how different metals react in different ways, for instance, Fe^+ , Co^+ , and Ni^+ are more reactive than Cr^+ and Mo^+ in that Fe^+ , Co^+ and Ni^+ have stronger interactions with organic substrates and thus can rearrange the organic molecules to different products. Cr^+ and Mo^+ , on the other hand, seem to prefer to eliminate one or more molecules of H_2 , which is especially true for Mo^+ .

In order to gain some insight into the differences in chemistry of metal ions, an ab initio calculation on CrCH_2^+ is being pursued and will be discussed in the next section.

AB INITIO CALCULATION

C. AB INITIO CALCULATIONS

1. Introduction

I. The Importance of Ab Initio Calculations:

In the last section (B.5), we have seen that Fe^+ , Co^+ , and Ni^+ exhibit similar chemistries in their reactions with most of the organic compounds used, and Cr^+ , Mo^+ and W^+ fall into another group, which exhibit quite different chemistries in their reactions with the same organic compounds. However, we can not understand the bonding behavior of these metal ions in terms of their orbitals, orientation, size and symmetry as those listed at the beginning of section B.5 from these studies. Note that the reaction products we have observed from ICR studies are mass peaks. Therefore the assignments of ion structures of these products are sometimes ambiguous, although the double resonance technique, the CID (collisionally induced dissociation) technique and the use of the labelled compounds can sometimes give helpful information. It is important to do the ab initio calculations so that we can obtain insights into the nature of the bond between the metal and substrate.

Fe^+ , has a ground state, ^6D , corresponding to an $[\text{Ar}] 4s^1 3d^6$ configuration¹⁵⁷. Cr^+ has a ground state¹⁵⁷ ^6S , corresponding to $[\text{Ar}] 3d^5$. However, there is some evidence^{141,148} for the presence in the gas phase of its next excited state ^6D ($4s 3d^4$) at 1.47 eV. It is not surprising that $\text{Cr}^+(^6\text{S})$ will form an addition complex with 12-crown-4

electrostatically. To form covalent bonds with ligands, it presumably needs to use its 4s orbital. On the other hand, Cr^+ (^6D) might be able to form covalent bonds with ligands by use of sp hybrid orbitals. Ni^+ has a ground state ^2D , corresponding to the $[\text{Ar}] 3\text{d}^9$ configuration¹⁵⁷ and there is no evidence that its next excited state ^4F at 1eV (corresponding to $[\text{Ar}] 4\text{s}^1 3\text{d}^8$ configuration) participates in the gas phase chemistry. Thus Ni^+ (^2D) will interact with ligands electrostatically and form the addition complexes with TDE, 12-crown-4 and 15-crown-5. It can also interact with ligands covalently by use of its s and d orbitals^{†163} or sp hybrid orbitals by promoting to ^4F state^{‡123,164,165}.

[†] Ni^+ has a ground state of $[\text{Ar}] 3\text{d}^9$. To form a covalent bond with a ligand, a d orbital has to be involved in bonding, or it may mix with a s orbital to form a sd hybrids, or Ni^+ could be experiencing the configuration mixing of $[\text{Ar}] 3\text{d}^9$ and $[\text{Ar}] 4\text{s} 3\text{d}^9$, as a result of positive charge¹⁵⁴ on the metal center. CID spectra of some product ions in the reactions of Co^+ with alkanes conducted in our laboratory¹⁶⁶ also indicated that there are more than two different structures at the same mass unit, which might be derived from the reactions of different electronic configurations of the metal ion.

[‡] Note that Kunz concluded the 4s^2 bonding to H by use of sp hybrids for all the first transition metals. Later, Walch *et. al.* correlated the s orbital with p orbitals, ending up with a much d character in ScH with $^1\Sigma^+$ as its ground state. However, its next excited state, 3Δ which is the ground state from Kunz's calculation is only 4.6 kcal/mole above $^1\Sigma^+$ ground state.

II. Review of Ab Initio Calculations of Transition Metal Compounds.

From spectroscopic studies, P.R. Scott and W.G. Richards¹⁵⁰ concluded that three types of configurations are important in the monhydride, and they may be loosely described as s^2d^{n-2} , sd^{n-1} and d^n . In ScH and TiH, the s^2d^{n-2} is important. From TiH to FeH, the sd^{n-1} configuration always gives rise to ground state; however, the d electrons are largely non-bonding in these compounds. However, in NiH the s-orbital contribution is still not negligible. In the second transition series, the d-orbitals are relatively less stable, and PdH may be understood in terms of simple covalent bonding between 4d- and 1s orbitals alone[†].

However, recent ab initio calculation¹⁵¹ shows that ScH has a tremendous amount of $d\sigma$ bonding in the ground state. S.P. Walch¹⁵¹ incorporated atomic correlation terms leading to an accurate $4s^2 3d^8$ - $4s^1 3d^9$ separation for the Ni atom into all electron MCSCF/CI calculations for the $X^2\Delta$ state of NiH and found that although the bonding in NiH is predominantly $4s^1 3d^9$ like, $4s^2 3d^8$ like configurations are found to be important in the small R region, and he expects that

[†] 3d orbital is only 30% size of 4s orbital. Hence, there will be poor overlap of 3d with ligands; 4s on the other hand will form bonds easily. In contrast, 4d has 60% size of 5s orbital (electron density distribution), which then makes it possible to bond by use of a $4d_z$ orbital.

a mixture of $4s^2 3d^n$ and $4s^1 3d^{n+1}$ to be important in most transition metal bonds except for Mn where $4s^1 3d^6$ is too high to be accessible for bonding¹⁵². From other calculations on systems, such as NiH, NiCH₂, NiCH₃, NiCO¹⁶³, CrCH₂, CrH¹⁵⁴, it was concluded that the s orbital is important in bonding with only a small contribution from d orbital or a weak d bonding. To form a π bond, the ligand has to get closer to the metal, and the strong repulsive interaction with 4s orbital in the $4s^2 3d^n$ configuration will avoid this energy lowering process, unless the 4s orbital mixes with 4p to become two 4s 4p hybrids as in NiCH₂. Also, model studies of π -bonded organometallic systems Mn-C₂H₂ and Mn-C₂H₄ are calculated to have small bonding energy, < 10 kcal; Ni-C₂H₂ is bound by $\approx$ 20 kcal, and Steigerwald and Goddard calculated the Cp₂Ti(C₂H₄) and Cl₂Ti(C₂H₄) systems and found that metallocycle form is more stable than π -bonded form by C₂H₄.

On the other hand, MnCH₂⁺ and CrCH₂⁺¹⁵⁵ were calculated to have the very similar ground state molecular orbitals, they all use M⁺ 4s to bond the methylene 3a₁ orbital although Mn⁺ has a $4s^1 3d^5$ ground configuration, while Cr⁺ is $3d^5$. CrCH₂⁺ seems to be similar¹⁵⁴.

Further, the ligand has a strong influence on the metal center for its bonding to another ligand^{124,156}. It turns out that the change of the electronic configuration of a metal center used for bonding might be crucial as we keep

putting ligands on it. In the solid state, if we keep adding electrons into ZnS sytem to become GaSe then CuPbS and then As system, we will see some bonds broken in the unit cell to become different structures. Therefore, the strategy that Beauchamp¹²³ used in relating promotion energy, from $3d^n$ to $4s^1 3d^{n-1}$, to bond energy between first transition metal ions and simple ligands has still to be scrutinized as ligands are changed to the multifunctional molecules, since the transition states or intermediates of the metal ion molecule reactions might involve many ligands to be bonded to the metal center.

III. Theory of Ab Initio Calculations

Although there are a growing number of ab initio calculations published in the past two decades¹⁷², very few of them were devoted to the understanding of univalent metal ion-ligand species. There are some books available for discussing the theories in ab initio calculations¹⁷³⁻¹⁷⁷. However, a brief review will be discussed in the following.

From quantum mechanics, a total wave function of an atom can sometimes be expressed by a Slater determinant. For example, the lithium atom can be written as

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} \phi_{1s} (1) & \overline{\phi_{1s} (1)} & \phi_{2s} (1) \\ \phi_{1s} (2) & \overline{\phi_{1s} (2)} & \phi_{2s} (2) \\ \phi_{1s} (3) & \overline{\phi_{1s} (3)} & \phi_{2s} (3) \end{vmatrix}$$

or in a simpler form of

$$\psi = \begin{vmatrix} \phi_{1S} & \overline{\phi_{1S}} & \phi_{2S} \end{vmatrix}$$

where ϕ 's are one-electron wave functions (spin orbitals).

In most calculations the orbital ϕ is expanded in terms of a set of basic functions,

$$\phi = \sum_i C_i X_i$$

Our problem is to determine the coefficient C_i . The X_i can be chosen to form an orthonormal set,

$$\int X_i^2 dV = 1$$

$$\int X_i X_j dV = 0 \quad \text{for } i \neq j$$

but in practice it is more convenient if they are normalized but not orthogonal, i.e.

$$\int X_i^2 dV = 1,$$

but

$$\int X_i X_j = S_{ij}.$$

Thus the wave function of the molecule Ψ can be broken down as follows:

$$\Psi = \mathcal{Q}\psi \quad ; \quad \mathcal{Q} \text{ is an antisymmetrizing operator,}$$

$$\psi = \phi_1 \phi_2 \dots \phi_n \quad ; \quad \phi \text{ is a one electron spin orbital.}$$

Thus although the use of the variation principle for the molecule will involve us in calculating the integrals $\langle \Psi | H | \Psi \rangle$ and $\langle \Psi | \Psi \rangle$, these can be broken down into integrals involving the orbitals, which in turn reduce, or expand to atomic integrals involving the basic function χ_i .

In writing the electronic Hamiltonian equations, there is considerable advantage if one works in atomic units, in which $\hbar$ (planck's constant divided by 2π), the electronic charge e , and the electron mass m_e are all unity. Also, the distance is given in bohr radii a_0 (bohrs), where 1 bohr is 0.52918×10^{-8} cm or $0.52918 \text{ \AA}$. The unit of energy is the Hartree, equal to 27.21 eV or 627.5 kcal/mole and is equal to e^2/a_0 .

The rigorous mathematical expression of the molecular orbital model is the Hartree-Fock (HF) approximation. For closed-shell atoms and molecules the HF wave function is of the form

$$\psi_e = A(n) \phi_1(1)\phi_2(2)\dots\phi_n(n) \quad (1.1)$$

and is conveniently written as a Slater determinant:

$$\psi_e = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1) & \phi_2(2) & \dots & \phi_n(n) \end{vmatrix} \quad (1.2)$$

For a given geometry of a particular molecule in a closed-shell state, any number of different Slater determinates may be used as approximate wave functions. However, there is

only one HF determinant, namely that for which the orbitals ϕ_i in Eq. (1.1) have been varied to give the lowest possible energy.

By minimizing the energy resulting from the single determinant wave function in Eq. (1.2) one can derive a rather complicated set of integrodifferential equations, the HF equations. The HF wave function is the best wave function which can be constructed by assigning each electron to a separate orbital. For molecules, each ϕ_i can be expanded in terms of the basis functions χ_i and the best (lowest energy) single determinant wave function constructed within a finite basis set is the self-consistent-field (SCF) wave function. For example, the wave equation of molecular H_2 may be written in atomic units as

$$\left\{ -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} \right\} \Psi = E \Psi$$

or in a simplified form

$$\{H_{(1)}^N + H_{(2)}^N + \frac{1}{r_{12}}\} \Psi = E \Psi \quad \text{where } H_{(1)}^N \text{ is a hydrogen-}$$

molecule ion Hamiltonian. In the notation introduced earlier the wave function for H_2 can be written as a Slater determinant of

$$\Psi = \frac{1}{\sqrt{2}} |1\sigma_g \quad \overline{1\sigma_g}| = \frac{1}{\sqrt{2}} [1\sigma_g(1) \overline{1\sigma_g}(2) - 1\sigma_g(2) \overline{1\sigma_g}(1)]$$

The molecular orbital $1\sigma_g$ could be expressed in LCAO

form as $\phi_{1\sigma_g} = \frac{1}{\sqrt{2(1+S)}} (1 S_A + 1 S_B)$, where S is the overlap integral and is defined as $\int \phi_{1sA} \phi_{1sB} dz$. However we may add even more terms to this expansion of $\phi_{1\sigma_g}$, e.g.,

$$\phi_{1\sigma_g} = C_1 1 S_A + C_2 1 S_B + C_3 2 S_A + C_4 2 S_B + C_5 2 P_{xA} + \dots$$

The energy of the ground state is $\langle \Psi | H | \Psi \rangle$ and can be expressed as,

$$E (H_2: {}^1\Sigma_g^+) = 2\varepsilon_{1\sigma_g}^N + J_{1\sigma_g 1\sigma_g}$$

where $\varepsilon_{1\sigma_g}^N$ is the energy of one electron in a molecule and is defined as $\int \phi_{1\sigma_g}^* (1) H_1^N \phi_{1\sigma_g} (1) dV_1$ and J is a coulomb integral and is defined as

$$\iint \phi_{1\sigma_g}^* (1) \phi_{1\sigma_g}^* (2) \frac{1}{r_{12}} \phi_{1\sigma_g} (1) \phi_{1\sigma_g} (2) dV_1 dV_2 =$$

$$\iint \phi_{1\sigma_g}^2 (1) \frac{1}{r_{12}} \phi_{1\sigma_g}^2 (2) dV_1 dV_2$$

(assuming the orbitals are real).

More generally, the energy is a sum of one-electron, coulomb, and exchange terms

$$E = \sum_i \varepsilon_i^N + \sum_{i < j} \iint \phi_i^2 (1) \frac{1}{r_{12}} \phi_j^2 (2) dV_1 dV_2$$

$$- \sum_{i < j}' \iint \phi_i (1) \phi_j (1) \frac{1}{r_{12}} \phi_i (2) \phi_j (2) dV_1 dV_2$$

where the last term is a sum of exchange integrals.

The resulting equations after minimizing the energy (variation theorem) are

$$\{H^N + \sum_{j=1}^n \int \phi_j^2 (1) \frac{1}{r_{12}} dV_2\} \phi_i(1) -$$

$$\{ \sum_{j=1}^n \int \phi_j(2) \phi_i(2) \frac{1}{r_{12}} dV_2 \} \phi_j(1) = \epsilon_i^{SCF} \phi_i(1)$$

or, in the shorthand form,

$$\{H^N + \sum_j J_i - \sum_j' K_j\} \phi_i(1) = \epsilon_i^{SCF} \phi_i(1)$$

or, in an even more compact form we may write

$$H^{SCF} \phi_i(1) = \epsilon_i^{SCF} \phi_i(1)$$

Now if $\phi_i = \sum_n C_{in} X_n$

then $H^{SCF} \sum_n C_{in} X_n = \epsilon_i^{SCF} \sum_n C_{in} X_n$

By multiplying both sides of this equation by X_m and integrating over all space, we get

$$\sum_n C_{in} (H_{mn}^{SCF} - \epsilon_i^{SCF} S_{mn}) = 0$$

or

$$\det \left| H_{mn}^{SCF} - \epsilon_i^{SCF} S_{mn} \right| = 0$$

If H_{mn}^{SCF} and S_{mn} could be calculated the secular determinant could be solved directly for the eigenvalues, the SCF orbital energies ϵ_i^{SCF} . However, both H_{mn} and S_{mn} demand a knowledge of the wave functions we are trying to find and

the solution has to be iterative, which makes the use of a computer mandatory.

For example, in LiH, the structure for Li is $1s^2 2s$ and H is $1s$, and

$$\Psi(\text{LiH} ; \chi^1 \Sigma^+) = | 1\sigma^2 2\sigma^2 |$$

now

$$\phi_{1\sigma} = C_1 1s_{\text{Li}} + C_2 1s_{\text{H}} + C_3 2s_{\text{Li}} + \dots$$

In outline, our procedure might be:

1. Guess some values of the C's
2. Calculate all the various atomic integrals and hence build up $H_{i\sigma j\sigma}^{\text{SCF}}$ and $S_{i\sigma j}$
3. Solve the determinantal equation giving the possible values of ϵ_i^{SCF}
4. Substitute these in the secular equations giving new C's
5. Go back to stage 1 and repeat until the values of ϵ_i^{SCF} or the C's converge to steady values within an arbitrary threshold ($\sim 10^{-6}$) and then take the values of the converged C's.

The result of this will be to provide SCF orbitals, both occupied and unoccupied: that is to say the coefficients in

$$\phi_{i\sigma} = C_{i1} 1s_{\text{Li}} + C_{i2} 1s_{\text{H}} + C_{i3} 2s_{\text{Li}} + \dots \text{ and } \epsilon_i^{\text{SCF}}$$

For open - shell SCF methods, both Roothaan's¹⁷⁸ and

Nesbet's¹⁷⁹ method are used in an attempt to eliminate the off-diagonal terms $\epsilon_{ij}^{\text{SCF}}$ which cannot be completely eliminated by means of unitary transformations.

The secular equations may be simplified by the symmetry considerations. The role of symmetry enters the calculations in the following way:

1. It enters the integral calculation and the basic function transformation^{188,189}.

2. It enters SCF calculation. Linear combination of basic functions for different irrerepresentation species will reflect the symmetry of the molecule. This will simplify the large matrices by reducing them to a series of blocks along the diagonal, one for each molecular orbital symmetry type. Also, the matrices can be simplified by the use of symmetry operator.

3. It enters MCSCF and CI calculations. By mixing configurations having the same symmetry, the matrices in both calculations can be simplified¹⁹⁰.

Before going to the next section, some important concepts used in ab initio calculations are summarized in the following:

1. The solution of the HF equations including symmetry and equivalence restrictions yields the restricted Hartree-Fock (RHF) wave function. By removing the symmetry and equivalence restrictions placed on RHF wave functions, single-determinant wave functions of lower energy can frequently be obtained.

2. Electron correlation. In the HF approximation, the motion of each electron is solved for in the presence of the average potential created by the remaining (n-1) electrons. The contribution to the total energy due to instaneous repulsions is called correlation energy¹⁸⁰. The most frequently used method for approaching the electron correlation problem is configuration interaction (CI), which is just a linear combination of configurations with coefficients variationally determined. More precisely, the CI wave function is of the form,

$$\psi_e = \sum_i C_i \phi_i$$

where the ϕ 's are an orthonormal set of n electron configurations. The coefficients C_i are determined to minimize the energy $\int \psi_e^* H_e \psi_e dz$. Application of the variation principle leads to

$$\det \left| H_{ij} - \epsilon_i^{CI} S_{ij} \right| = 0 \quad (1.3)$$

where $H_{ij} = \int \phi_i^* H_e \phi_j dz$ and is the matrix elements between configurations. Note that matrix elements H_{ij} between different configurations i and j are zero if i and j are of different symmetry. Therefore, the secular equation is greatly simplified by only considering configurations which have the total symmetry of the particular electronic state being investigated.

3. Multiconfiguration SCF (MCSCF). Solution of the eigenvalue problem in (1.3) will yield the optimum values of C_1 , C_2 , and C_3 . However, the wave function has not been variationally determined yet unless the spin-orbitals used in the configurations have also been varied to minimize the orbital energy. The MCSCF wave function is the best (lowest energy) wave function that can be obtained by simultaneously varying both the orbitals ϕ and the CI coefficients C . This regards to MCSCF calculations, which is again usually solved by the iterative technique¹⁸¹.

4. Basis sets. Molecular calculations are generally carried out in terms of basis functions centered on each atom in the molecule. A primary consideration in evaluating the reliability (i.e. in agreement with reality) of an electronic structure calculation is the basis set, in which both Slater and Gaussian functions are most frequently employed. Slater basis functions have the radial form

$$A r^{n-1} e^{-\xi r}$$

where A is a normalization factor, n is the principal quantum number, and ξ is the orbital exponent or screening parameter. Gaussian basis functions have the radial form,

$$B r^n e^{-\alpha r^2}$$

In principle one would probably prefer to use Slater functions in all molecular calculations. However, for

nonlinear polyatomic molecules the two-electron integrals (such as coulomb and exchange integrals) in terms of a slater basis set are extremely difficult to compute, while the same integrals in terms of gaussians may be evaluated comparatively simply and rapidly.

There are many different basis sets used depending on the systems we are dealing with.

a. The minimum basis set. It includes one function for each SCF-occupied atomic orbital with distinct n and ℓ quantum numbers. The functions of a minimum basis set are usually slater functions. The atom-optimized minimum basis set developed by Clementi¹⁸² may be used directly molecular calculations.

b. Double Zeta and extended basis sets. Usually, the minimum basis sets yield SCF energies above the HF energies. For this reason electronic structure calculation are frequently carried out with larger basis set. A double zeta includes exactly twice as many functions as the minimum basis. Any basis set of slater functions larger than double zeta are referred to be an extended basis set.

c. Contracted functions. As mentioned above, for big and nonlinear molecules, the use of gaussian functions are utilized to speed up computing the multicenter integrals, despite the fact that the number of gaussian functions is more than twice the number of slater functions. In order to save the computation time, the use of contracted

gaussinas¹⁸³⁻¹⁸⁵, i.e., linear combinations of gaussians with fixed coefficients is suggested. In solving the SCF equations, then, only the coefficients in each SCF orbital of the contracted functions must be determined. A notation of (10s 5p/3s 2p) means a basis set of ten s and five p (for example six 1s functions are used for 1s orbital, two 1s functions are used for 2s orbital and two 1s functions are used for 3s orbital and three 2p functions are used for 2p atomic orbital and another two 2p functions are used for 3p orbital) has been contracted to three s and two p functions.

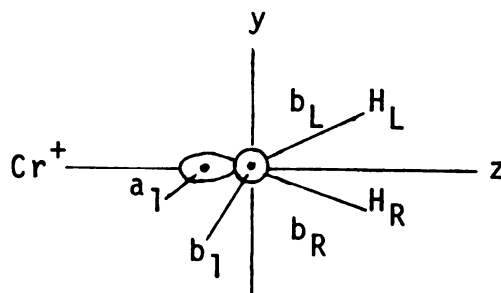
d. Polarization functions. In order to approach the HF energy limit, functions with higher ℓ values (d,f....) must be added to the basis when we are working on molecules. These functions with higher ℓ values being added are called polarization functions¹⁸⁶. A basis including (4s 2p 1d) on each first row atom and (2s 1p) on each hydrogen is referred to as double zeta plus polarization¹⁸⁷. Note that the double zeta level for a first row atom is (4s 2p).

The reliability of each basis set depends on the molecular properties we are dealing with. Therefore, the choice of the basis set is often based on experience.

2. Use of CrCH_2^+ As An Example of Ab Initio Calculation

In this section, a study of CrCH_2^+ will be given as an example of an ab initio calculation.

Assume Cr^+ interacts with CH_2 in a C_{2v} symmetry in the following coordinates:



where the various orbitals can be associated with the irreducible representations of C_{2v} character table¹⁹¹:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ	2	0	0	2		

By using the formula, $a_i = \frac{1}{h} \sum_R X(R) X_i(R)$ where h is the group order, $X(R)$ is the character of the matrix corresponding to operation R in the reducible representation, and $X_i(R)$ is any irreducible representation, we can get the symmetry species for the bonding orbitals b_L and b_R .

$$a_{A_1} = \frac{1}{4} (2 + 2) = 1 \text{ i.e., there is one } A_1 \text{ species}$$

$$a_{B_1} = \frac{1}{4} (2 + 2) = 1 \text{ i.e., there is one } B_2 \text{ species}$$

To determine orbitals corresponding to A_1 and B_2 , we use a projection operator¹⁹².

$$\begin{aligned}\hat{P}^{A_1} H_R &\approx (1) \hat{E} H_R + (1) \hat{C}_2 H_R + (1) \hat{\sigma}_v(xz) H_R + (1) \hat{\sigma}'_v(yz) H_R \\ &= H_R + H_L + H_L + H_R = 2 (H_R + H_L)\end{aligned}$$

$$\begin{aligned}\hat{P}^{B_2} H_R &\approx (1) \hat{E} H_R + (-1) \hat{C}_2 H_R + (-1) \hat{\sigma}_v(xz) H_R + \hat{\sigma}'_v(yz) H_R \\ &= H_R - H_L - H_L + H_R = 2 (H_R - H_L)\end{aligned}$$

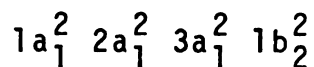
Hence, the sum of H_R and H_L belongs to the A_1 irreducible representation and the difference of H_R and H_L to the B_2 irreducible representation. By consulting the character table of C_{2v} symmetry, we have the following correspondence:

$$\begin{array}{lcl} A_1 & \left\{ \begin{array}{l} 1s^C \rightarrow 1a_1 \\ 2s^C \rightarrow 3a_1 \\ 2p_z^C \\ 1s_L^H + 1s_R^H \end{array} \right\} & \rightarrow 2a_1 \\ B_2 & \left\{ \begin{array}{l} 2p_y^C \\ 1s_R^H - 1s_L^H \end{array} \right\} & \rightarrow 1b_2 \quad B_1: 2p_x^C \rightarrow 1b_1\end{array}$$

Since two orbitals having almost the same energy and symmetry can form a bond, the $2p_z^C$ may form a bonding orbital with $1s_L^H + 1s_R^H$ and $2p_y^C$ may form another bonding orbital with $1s_R^H - 1s_L^H$. Therefore the electronic configuration of CH_2 in the ground state 3B_1 can be described as

$$1a_1^2 2a_1^2 3a_1 1b_2^2 1b_1 (^3B_1)$$

where carbon has $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$ configuration. On the other hand, if carbon uses $1s^2 2s^2 2p_y^1 2p_z^1$ configuration, we will have the electronic configuration of CH_2 as,



which is the first excited state of 1A_1 symmetry.

Keeping this idea in mind, we will have the following species:

<u>species</u>	<u>ground state</u>	<u>first excited state</u>
Cr^+	$1s^2 2s^2 2p^6 3s^2 3p^6, 3d^5(^6S)$	$1s^2 2s^2 2p^6 3s^2 3p^6, 4s^1 3d^4(^6D)$
CH_2	$1a_1^2 2a_1^2 1b_2^2 3a_1 1b_1 (^3B_1)$	$1a_1^2 2a_1^2 3a_1^2 1b_2^2 (^1A_1)$

There are 23 electrons in Cr^+ , 18 electrons are in the Ar core and 5 electrons are valence. There are 8 electrons in CH_2 , 6 electrons are in the "core" and there are only 2 "valence" electrons. Therefore, the symmetry adapted core molecular orbitals can be described as

<u>"core" orbitals</u>	<u>Cr^+ contributions</u>	<u>CH_2 contribution</u>
$1a_1 \dots \dots \dots 7a_1$	$1s, 2s, 2p_z, 3s, 3p_z$	$1s_C, b_R + b_L$
$1b_1 \ 2b_1$	$2p_x, 3p_x$	none
$1b_2 \ 2b_2 \ 3b_2$	$2p_y, 3p_y$	$b_R - b_L$

and leave 7 valence electrons for bonding between Cr^+ and CH_2 .

By symmetry, we have the following states when we leave Cr^+ in C_{2v} symmetry.

<u>states of Cr^+ in an isolated atom</u>	<u>states of Cr^+ in C_{2v} symmetry</u>
$^6S (d^5)$	6A_1
$^6D (sd^4)$	$2\ ^6A_1 + ^6B_1 + ^6B_2 + ^6A_2$

Note that there are five states in C_{2v} symmetry when Cr^+ is in its first excited state, because D has $\ell = 2$, and the number of states is given by $2\ell + 1 = 5$. In other words, there are five different ways of distributing one s and d orbitals, each gives corresponding state.

Now, if we leave Cr^+ and CH_2 in C_{2v} symmetry at ∞ separation, we will have even more possible states, which are summarized below:

<u>Cr^+</u>	<u>CH_2</u>	<u>$(\text{Cr} - \text{CH}_2)^+$ at ∞ separation¹⁹³</u>
6S	3B_1	$^8B_1, ^6B_1, ^4B_1$
6S	1A_1	6A_1
6D	3B_1	$2\ ^{8,6,4}B_1 + ^{8,6,4}A_1 + ^{8,6,4}A_2 + ^{8,6,4}B_2$
6D	1A_1	$2\ ^6A_1 + ^6B_1 + ^6B_2 + ^6A_2$

Since the 1A_1 state of CH_2 has an electron pair located on the z axis, when CH_2 approached to Cr^+ , in an effort to make a bond with it, these paired electrons might experience strong repulsion from the d electrons of Cr^+ . We think that this interaction will be repulsive and it is therefore

reasonable to disregard any states arising from the combination of 1A_1 of CH_2 with ground state Cr^+ .

If we consider the first situation, $^6S + ^3B_1$ and the states which evolve from the 8B_1 , 6B_1 and 4B_1 , we will have no bond, one bond and possible double bond respectively.

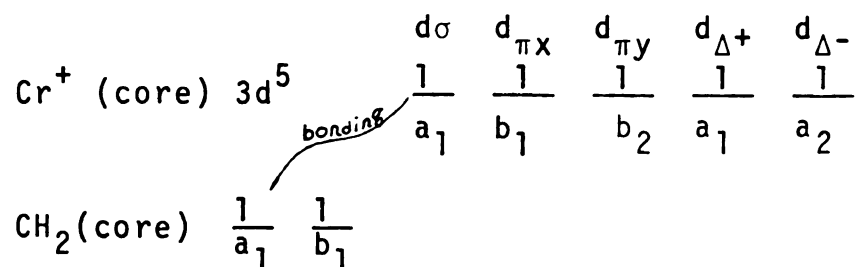
8B_1 - there are 7 unpaired electrons with the same spin, and it is unlikely to be bound, i.e. no bond will form.

6B_1 - there are five unpaired electrons, i.e., there is one singlet couples pair. Hence, the possible chemical bond at large separation must be due to the orbital overlap between 3 $d\sigma$ of Cr^+ and σ orbital of CH_2 .

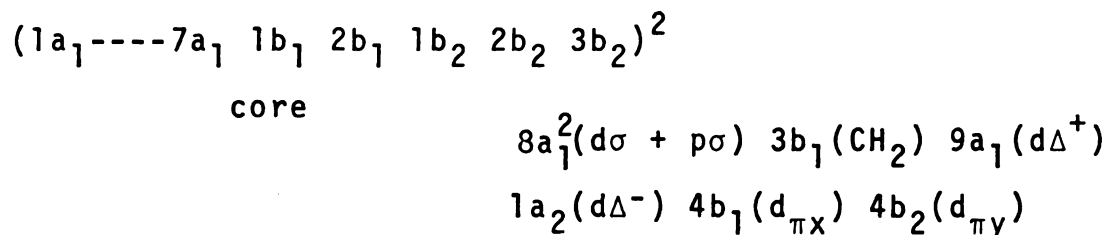
4B_1 - there are three unpaired electrons, i.e., there are two singlet coupled pairs and hence a possible double bond exists.

Therefore, the calculation will focus on the 6B_1 and 4B_1 states. However, we have to remember that $^6D + ^3B_1$ and $^6D + ^1A_1$ asymptotes also contribute states of these symmetries. While these are noninteracting at ∞ separation, they may interact strongly as the distance R decreases to the equilibrium value.

The 6B_1 state arises from one bond formed by $Cr (^6S)$ and $CH_2 (^3B_1)$. Consider the valence electrons of both Cr^+ and CH_2 in this state.



where $d\sigma$ denotes d_{z^2} ; $d_{\pi x}$ denotes d_{xz} and $d_{\pi y}$ denotes d_{yz} ; d_{Δ^+} denotes $d_{x^2-y^2}$ and d_{Δ^-} denotes the d_{xy} orbital with $|m_l| = 0, 1, 2$ respectively. Also, the symmetry of each orbital can be found from the character table. Now, if a sigma bond is formed between $d\sigma$ of Cr^+ and $p\sigma$ of CH_2 (both have the same irreducible representation a_1), then by taking into account the core orbitals, the molecular orbitals of CrCH_2^+ at infinite separation can be described as:



In order to carry out reliable ab initio calculation, good basis functions have to be chosen for each atom. The Cr^+ basis functions used in the CrCH_2^+ calculation are from Wachters, i.e., (14 s, 11p, 6d/ 5s 4p 3d). The carbon basis (11s, 6p/3s 2p) is from Duijneveldt and the hydrogen basis (4s/2s) is from Huzenaga. In all 120 primitive gaussians are used to form 48 contracted orbitals over 4 centers. For convenience, each basis function is given by a number

so that they are easy to read. The basis functions used in CrCH_2^+ are the following.

1	1s	21	xz	41	y_C
2	2s	22	xz'	42	y'_C
3	3s	23	xz''	43	z_C
4	4s	24	yz	44	z'_C
5	5s	25	yz'	45	s_{HR}
6	x	26	yz''	46	s'_{HR}
7	x'	27	xx	47	s_{HL}
8	x''	28	xx'	48	s'_{HL}
9	x'''	29	xx''		
10	y	30	yy		
11	y'	31	yy'		
12	y''	32	yy''		
13	y'''	33	zz		
14	z	34	zz'		
15	z'	35	zz''		
16	z''	36	s_C		
17	z'''	37	s'_C		
18	xy	38	s''_C		
19	xy'	39	x_C		
20	xy''	40	x'_C		

where x, x' , x'' and x''' basis functions are used to stand for the p_x orbitals of chromium, and y, y' , y'' , y''' are for the p_y orbitals of chromium, etc. xy, xy' , xy'' , xz, xz' , xz'' ---

zz" are used to build up the 3d orbitals of chromium.

Number 36 to 44 are used for s , p_x , p_y and p_z wave functions of carbon and s_{HR} , s'_{HR} are used for s wave functions of Hydrogen atom H_R and s_{HL} , s'_{HL} are used for s wave functions of Hydrogen atom H_L .

Moreover, these basis functions can be catagorized to four irreducible representations in C_{2v} character table according to their symmetry characters by the use of the same method used on page 212. Hence, we have the following arrangements

<u>1</u>	A_1 Symmetry (22)	<u>2</u>	B_2 Symmetry (11)
1	1	23	10
2	3	24	11
4	4	25	12
5	5	26	13
6	14	27	24
7	15	28	25
8	16	29	26
9	17	30	41
10	2 x 33 - 27 - 30	31	42
11	2 x 34 - 28 - 31	32	45 - 47
12	2 x 35 - 29 - 32	33	46 - 48
13	27 - 30	<u>3</u>	B_1 Symmetry (9)
14	28 - 31	34	6
15	29 - 32	35	7
16	36	36	8

17	37	37	9
18	38	38	21
19	43	39	22
20	44	40	23
21	45 + 47	41	39
22	46 + 48	42	40
		<u>4</u>	<u>A₂ symmetry (3)</u>
		43	18
		44	19
		45	20

Thus, the 48 basis functions are reduced to 45 symmetry orbitals after taking into account the symmetry in a C_{2v} system. Note that the first and third column label the orbital numbering which is the computer readable form. For example, orbital 28 is actually the basis function 25 (yz') and is $6b_2$ in C_{2v} symmetry (Note that each symmetry species starts at 1). Similarly, orbital 21 is actually the sum of basis function 45 and 47, namely $s_{HR} s_{HL}$, and is $21 a_1$ in C_{2v} symmetry.

Therefore, the molecular electronic configuration of $CrCH_2^+$ described on page 217

$$(1a_1 \text{ --- } 7a_1 1b_1 2b_1 b_2 2b_2 3b_2)^2 8a_1^2 3b_1 9a_1 1a_2 4b_1 4b_2$$

can be written in an orbital numbering form by referring to the symmetry orbitals given above as

(1 2 3 4 5 6 7 34 35 23 24 25)² 8 8 36 9 43 37 26

or in a ordered form:

CORE: 1 2 3 4 5 6 7 23 24 25 34 35

VALENCE: 8 8 9 26 36 37 43

Table 21 lists the results of ab initio calculations of CrCH_2^+ at different electronic states.

3. Discussion

Figure 10, and 11 summarize the energy levels of different states from the ab initio calculations. At this level of calculations none of these states seem to form a bond between Cr^+ and CH_2 as that reported by Beauchamp¹⁴⁸ (65 ± 7 kcal/mole). As we can see from these figures that ${}^6\text{B}_1$ only forms a 12.5 kcal/mole bond at (2 x 2) SCF level, which includes the σ bond correlation. ${}^6\text{A}_2$ forms a 22.0 kcal/mole bond relative to excited state of $\text{Cr}^+({}^6\text{D})$ and ground state of $\text{CH}_2({}^3\text{B}_1)$. It doesn't co-relate to ground states of separated species and is thus not the ground state. On the other hand, ${}^4\text{B}_1$ gives a tremendously high energy at SCF level, reflecting the inadequacy of the SCF theory for this state. Correlating σ and π configurations to allow electrons more freedom, the energy is lowered. In fact, the lowest energy of this system is formed at bond separation $r = 1.85 \text{ \AA}$. However, its energy, -1082.02832 H shows no evidence of the presence of strong bond between ground

Table 21. Results Of Ab Initio Calculations Of CrCH_2^+

<u>$6B_1$</u>	<u>configuration</u>	<u>r</u>	<u>energy</u>	<u>comment</u>
	$(1a_1 - - - 7a_1 1b_1 2b_1 1b_2 2b_2 3b_2)^2 8a_1^2$ $3b_1 9a_1 1a_2 4b_1 4b_2$ (2 x 2)SCF	2.06Å	-1082.02350 H	SCF level
		2.06Å	-1082.03917 H	SCF + δ bond correlation
<u>$6A_2$</u>				
	$(1a_1 - - - 7a_1 1b_1 2b_1 1b_2 2b_2 3b_2)^2 8a_1^2$ $9a_1 10a_1 3b_1 4b_1 1a_2$ (2 x 2)SCF	2.06Å	-1082.00199 H	SCF
		2.06Å	-1082.01608 H	SCF + δ bond correlation
	+ (Core) $8a_1 11a_1 9a_1 10a_1$ $3b_1 4b_1 1a_2$ and electron spins	2.06Å	-1082.01886 H	CI
	+ (Core) $8a_1^2 12a_1 13a_1 3b_1 4b_1 1a_2$			
	+ (Core) $8a_1 10a_1 13a_1 3b_1 5b_1 1a_2$			
	+ (Core) $8a_1 10a_1 13a_1 3b_1 4b_1 2a_2$	2.06Å	-1082.0331 H	MCSCF (correlating d electron distributions)

Table 21 (con't)

<u>$6A_2$</u>	<u>configuration</u>	<u>r</u>	<u>energy</u>	<u>comment</u>
+ (Core)	$8a_1^2 12a_1 3b_1 5b_1 1a_2$			
+ (Core)	$8a_1^2 9a_1 12a_1 3b_1 4b_1 2a_2$			
+ (Core)	$8a_1^2 9a_1 10a_1 3b_1 5b_1 2a_2$			
<u>$4B_1$</u>				
(1a ₁ - - -	$8a_1 1b_2 2b_2 3b_2 1b_1 2b_1 3b_1)^2$	2.06Å	-1081.93022 H	
	$9a_1 4b_2 1a_2$			
(2 x 2)SCF		2.06Å	-1081.9398 H	SCF + δ bond correlation
(3 x 3)SCF		2.06Å	-1082.0100 H	SCF + δ + π bond correlation
				(allow the freedom of π electrons to move apart)
(3 x 3)SCF		1.85Å	-1082.018306 H	SCF + δ + π bond correlation
(3 x 3)SCF		1.70Å	-1081.99869 H	

CrCH_2^+ (${}^6\text{B}_1$ and ${}^6\text{A}_2$)
(Fixed at Schaefer's Geometry)

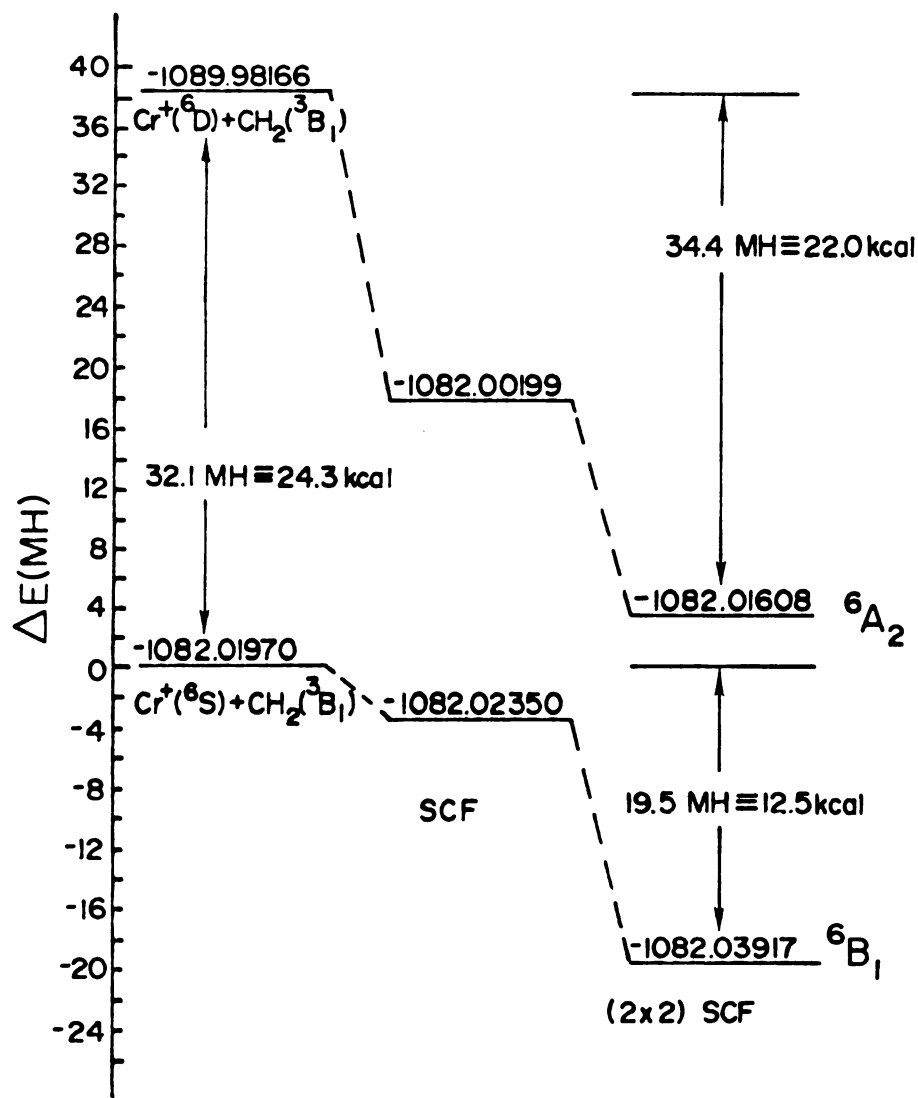


Figure 10. Energy Levels of ${}^6\text{B}_1$ And ${}^6\text{A}_2$ States Of CrCH_2^+

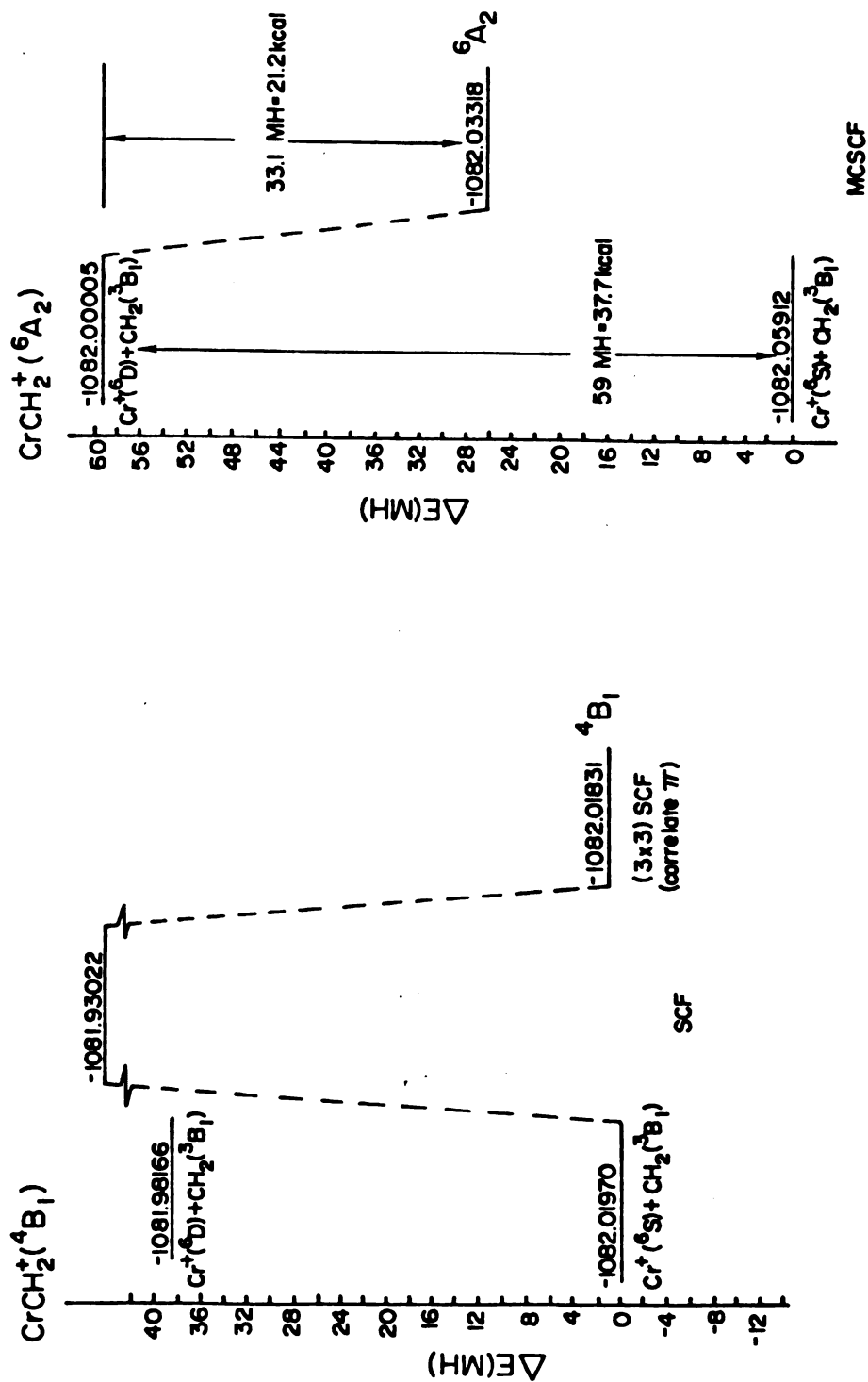


Figure 11. Energy Levels of 4B_1 And 6A_2 States of CrCH_2^+

state of $\text{Cr}^+(\text{}^6\text{S})$ and $\text{CH}_2(\text{}^3\text{B}_1)$, which is in contrast with Beauchamp's suggestion that CrCH_2^+ has a double bond. Beauchamp did suggest that if metal ions promote one electron into the s orbital, they will form a stronger bond with a ligand. This is borne out in this calculation since $\text{}^6\text{A}_2$ forms a 22 kcal/mole bond with respect to $\text{Cr}^+(\text{}^6\text{D})$ and $\text{CH}_2(\text{}^3\text{B}_1)$. One should however include d electron correlations at the MCSCF level and then compare with the same MCSCF level energy of separated species, i.e. $\text{Cr}^+(\text{}^6\text{S})$ and $\text{CH}_2(\text{}^3\text{B}_1)$.

Neither the $\text{}^6\text{B}_1$, nor the $\text{}^6\text{A}_2$ state is predicted to have comparable bond energy to the experimental value, although $\text{}^6\text{A}_2$ has the most energy lowering relative to excited state of $\text{Cr}^+(\text{}^6\text{D})$ and $\text{CH}_2(\text{}^3\text{B}_1)$, which somewhat matches Beauchamp's suggestion that essentially the bonding between the first row transition metal ions and ligands is via the metal's s electron. However, he pointed out that CrCH_2^+ doesn't fit in his plot of promotion energy (coordinate) versus bonding energy (abscissa). Perhaps the experiments he did do not refer to the bond energies of these high-spin electronic states of CrCH_2^+ . However, since the calculation of $\text{}^4\text{B}_1$ indicates a failure to form strong bonds, the experimental value is hard to refer to either ground state or the first excited state of Cr^+ and ground state of CH_2 . This may suggest another possible structure of CrCH_2^+ , for instance, $\text{H-Cr}^+-\text{C-H}$ instead of C_{2v} symmetry structure of CrCH_2^+ . The

possibility of forming bonds from excited state of CH_2 has been overlooked, because when it gets closer to Cr^+ , the paired electrons on CH_2 will experience a strong repulsive force. However, to check if it is possible to undergo a back bonding from d electrons of the Cr^+ , a ${}^6\text{A}_1$ state, derived from excited states of both $\text{Cr}^+({}^6\text{D})$ and $\text{CH}_2({}^1\text{A}_1)$ is being calculated. Other states derived from $\text{Cr}^+({}^6\text{D})$ and $\text{CH}_2({}^3\text{B}_1)$ have not been considered in this work. The reason being that other arrangements of four d electrons in five d orbitals of Cr^+ would not make the bonding dramatically different, neither would correlate the d electrons in MCSCF calculation, since the bonding is mostly contributed from 4s orbital of the Cr^+ and $3a_1$ orbital of the CH_2 .

Ab initio calculations provide considerable insight into the nature of the chemical bond since we can not only obtain the bond energies, but also orbital occupancies. Calculations of this sort might help us to understand the nature of transition metal insertion processes. For example, in order to understand how Cr^+ can split up H_2 molecule ($D(\text{H}-\text{H}) = 104.2 \text{ kcal/mole}$) to yield a low energy product, $\text{CrH}^+(D(\text{Cr}^+-\text{H}) = 35 \pm 4 \text{ kcal/mole})^{148}$ after putting the kinetic energy into Cr^+ . Ab initio calculations of CrH^+ and CrH_2^+ , are in progress.

APPENDICES

APPENDIX A.

Schematic Diagram For ICR Voltages Controls

There are two operating modes in ICR: normal drift mode and trapping mode.

In the normal drift mode, we want all drift plates and trap plates of the cell to be +15 V to -15 V (dc) adjustable. However, we need to pulse one trapping plate in both the source and the analyzer regions. Ions will have long residence times for reaction during positive pulse and are swept out of cell during the negative pulse. Also, the same pulsing will form a modulated signal out of the marginal oscillator, and then is input into the lock-in amplifier to be in phase with reference wave and consequently enhance the S/N ratio. This can be done by setting the mode switch to normal drift mode in Fig. 12. In this case, the monostable vibrator 74121 doesn't get a triggering pulse and Q will output a +5 V dc. As a result, both 2N404A PNP and 2N3053 NPN are switched off and output a +15 V dc as a +GATE pulse.

On the other hand, $\bar{Q}$ will send out a -5 V dc on a darlington pair of transistors on the other side, which will conduct both 2N404A PNP and 2N3053 NPN to output a -15 V dc as a -GATE pulse. Note that FETs need more than 10 Vs to drive, a regular TTL voltage cannot serve this purpose.

Hence, the FET at the bottom in Fig. 13 will always be ON and the drift potentials (adjustable) relative to the ground will appear on a drift plate after a voltage follower 741. Four of the same circuit will allow us to adjust four drift plates separately.

On the other hand, the comparator 311 in Fig. 14 will send out a pulse train whose pulse width is determined by voltage inputs to trigger the 74121 so that output 6 will give a TTL pulse train with pulse width adjustable by external RC values. When the pulse is at +5 V, both PNP and NPN transistors don't conduct and will output a +15 V at B, which will switch on N-channel FET (2N3819). Consequently, a reverse setting will then appear on the pulsed trapping plate (remember we put a unit gain of inverting amplifier in the front of 2N3819). When the pulse is at 0V, both PNP and NPN transistors will conduct to output a -15 V at point B, which will then turn on p-channel FET (2N3820) so that the voltage setting will appear on the pulsed trapping plate. In this way, we can have a voltage put on the pulsed trapping plate. Meanwhile, the voltage will always appear on the constant trapping plate.

In the trapping mode¹¹⁸, there are three pulsing sequence: trapping, detection and quench. Quench sequence can be combined in the detection step. For the trapping and detection period, we need to keep the trapping plates positively charged on both the source and analyzer. However, in

the trapping period, the source drift plates have to be at ground, and the analyzer drift plates have to be at negative potentials which can be done by adjusting the trapping potential as shown in Fig. 13. In the detection period, operation is set back to drift mode by putting a positive potential on the top drift plates and a negative potential on the bottom drift plates by adjusting the drift potential in Fig. 13. The necessary pulse timing for trapping and detection is provided again, by the circuit in Fig. 12. In order to be more versatile, input to pin 3 of the 311 comparator can be either a slow ramp for varied trapping and detection times or a constant voltage as shown in Fig. 16.

When pulse from Q output is at 0V, it will switch on both PNP and NPN transistors to give -15 V. When the pulse is at +5 V, it will switch off the PNP and NPN transistors to give +15 V at +GATE output as shown in Fig. 16. When the +GATE reaches +15 V, it will switch on the bottom FET in Fig. 13 and at the same time the -GATE is at -15 V to switch off the top FET. As a result, the drift potential will appear on drift plates for detecting ions. On the other hand, when +GATE is at -15 V, it will switch off the bottom FET. Meanwhile, -GATE will be at +15 V to switch on the top gate and the trapping potentials will appear on the drift plates for trapping the ions.

The trapping voltage in this mode can be set by switching the timing circuit in Fig. 14 to ground, which will

switch on both PNP and NPN transistors and will send out -15 V dc to point B which will drive P-channel FET 2N 3820 only so that a constant voltage appears on the pulse trapping plate. So now we have the same voltage going to both trapping plates. To be flexible, we can make two of the same circuits for both source and analyzer.

In the trapping mode, we also need a circuit to pulse the electron energy, this is done in Fig. 15. Q output (pin 6) of a 74121 will send out a pulse train to switch on and off the 2N 5415 PNP transistor so that it can pulse the electron energy and form ions, producing a modulated signal out of detector for S/N enhancement as described earlier.

As we can see from these circuit diagrams, all the timing pulses can be replaced by computer software programming using DACS. The computer setup for on line data acquisition is shown in Fig. 17. Where the setting circuit on the left bottom is for the mass calibration and circuit after ADC 0817 is for amplifying the signal and tailoring the analog signal to the safe values (≤ 5.12 V for PET). The software has been developed in our laboratory¹¹⁹.

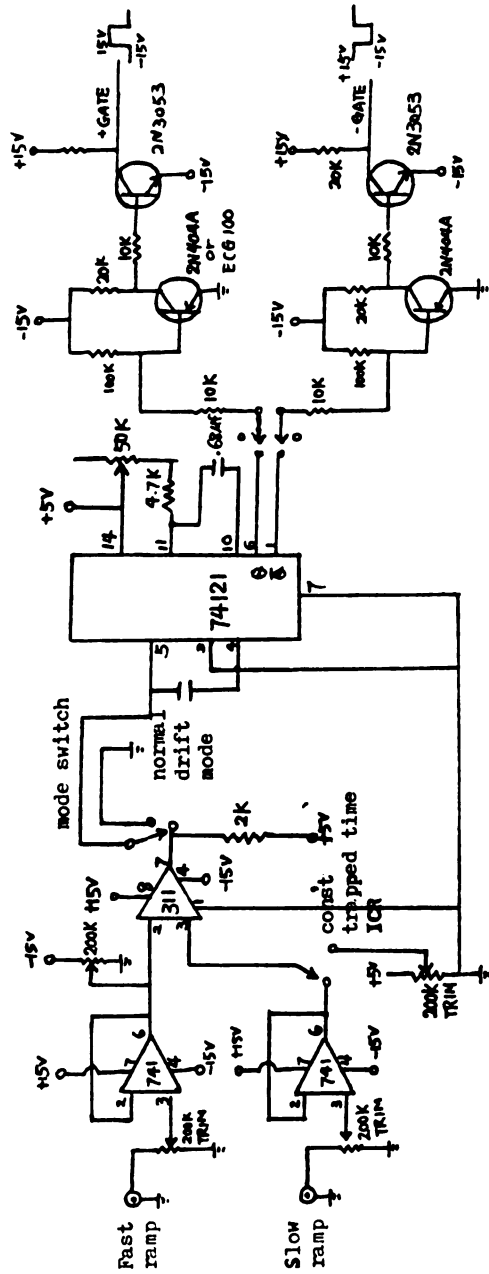


Figure 12. Trapped Ion Cell Circuitry---Pulsing Section.

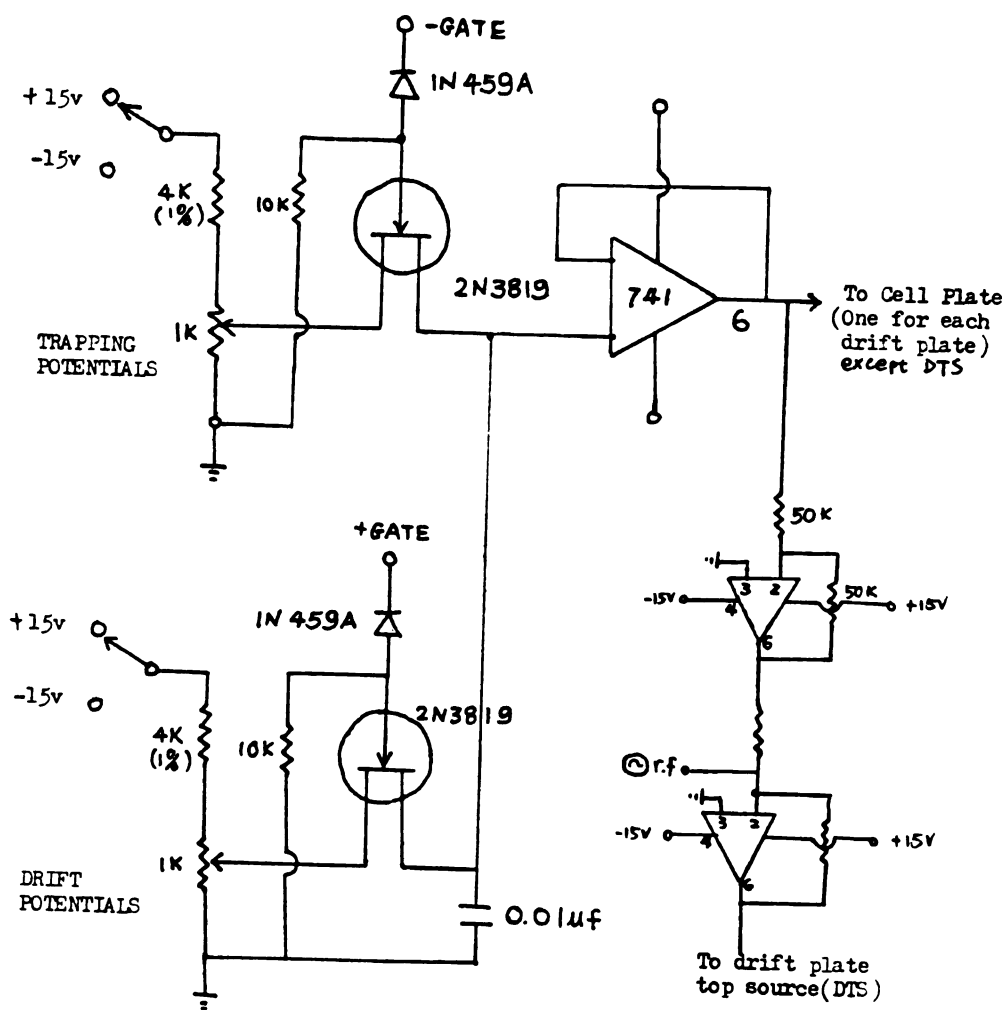


Figure 13. Trapped Ion Cell Circuitry----
Drift Section.

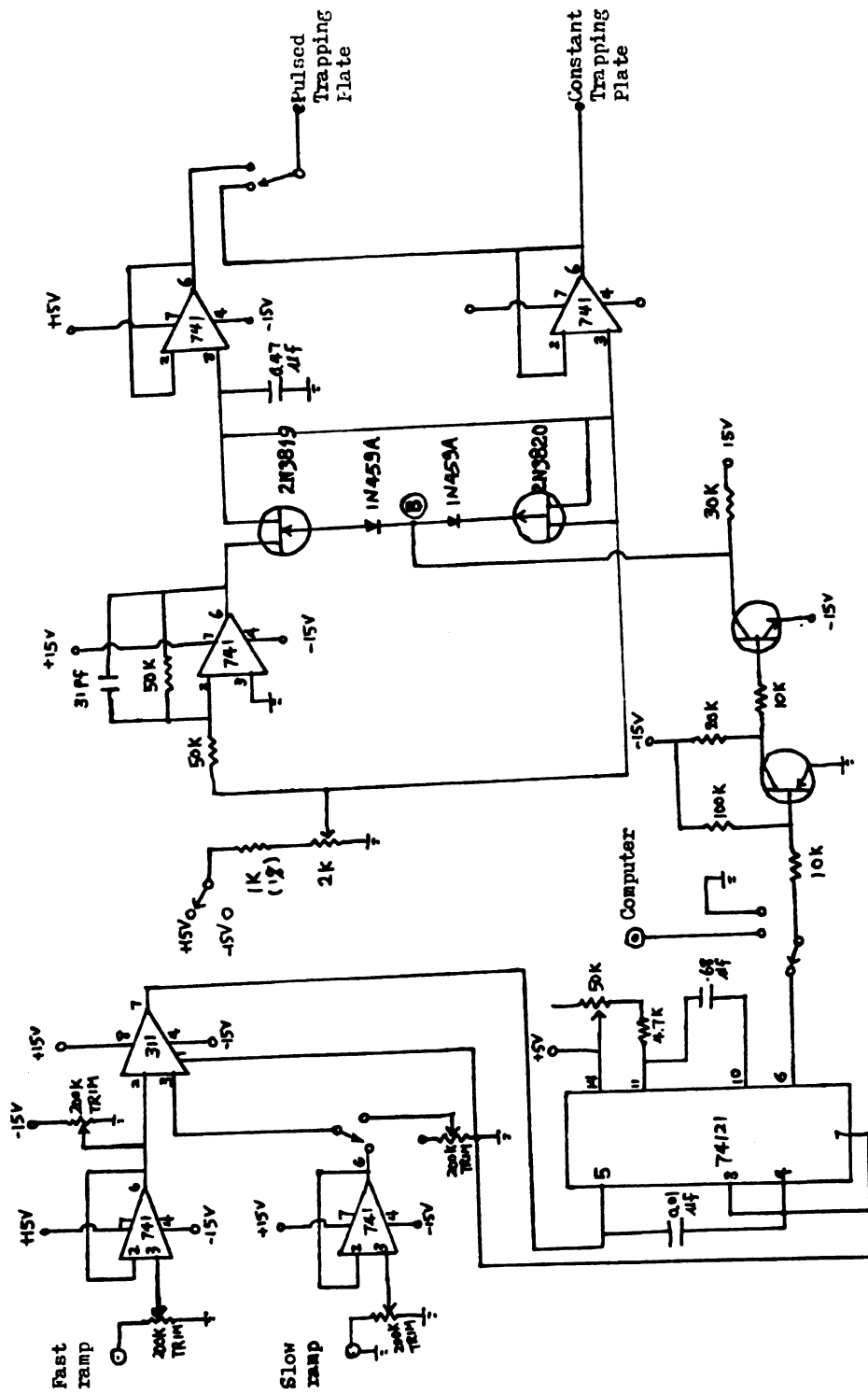


Figure 14. Trapped Ion Cell Circuitry---Trapping Section .

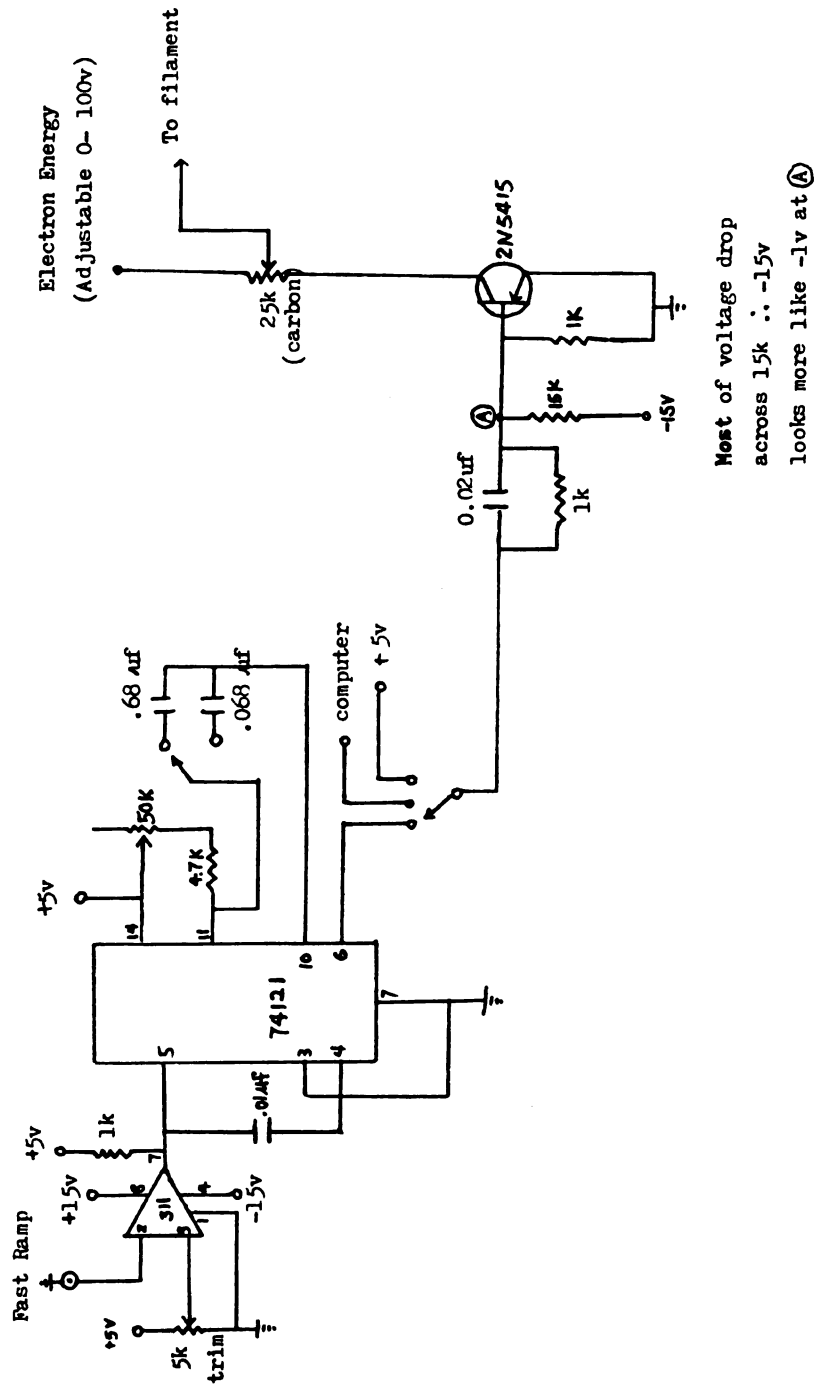


Figure 15. Electron Filament Bias

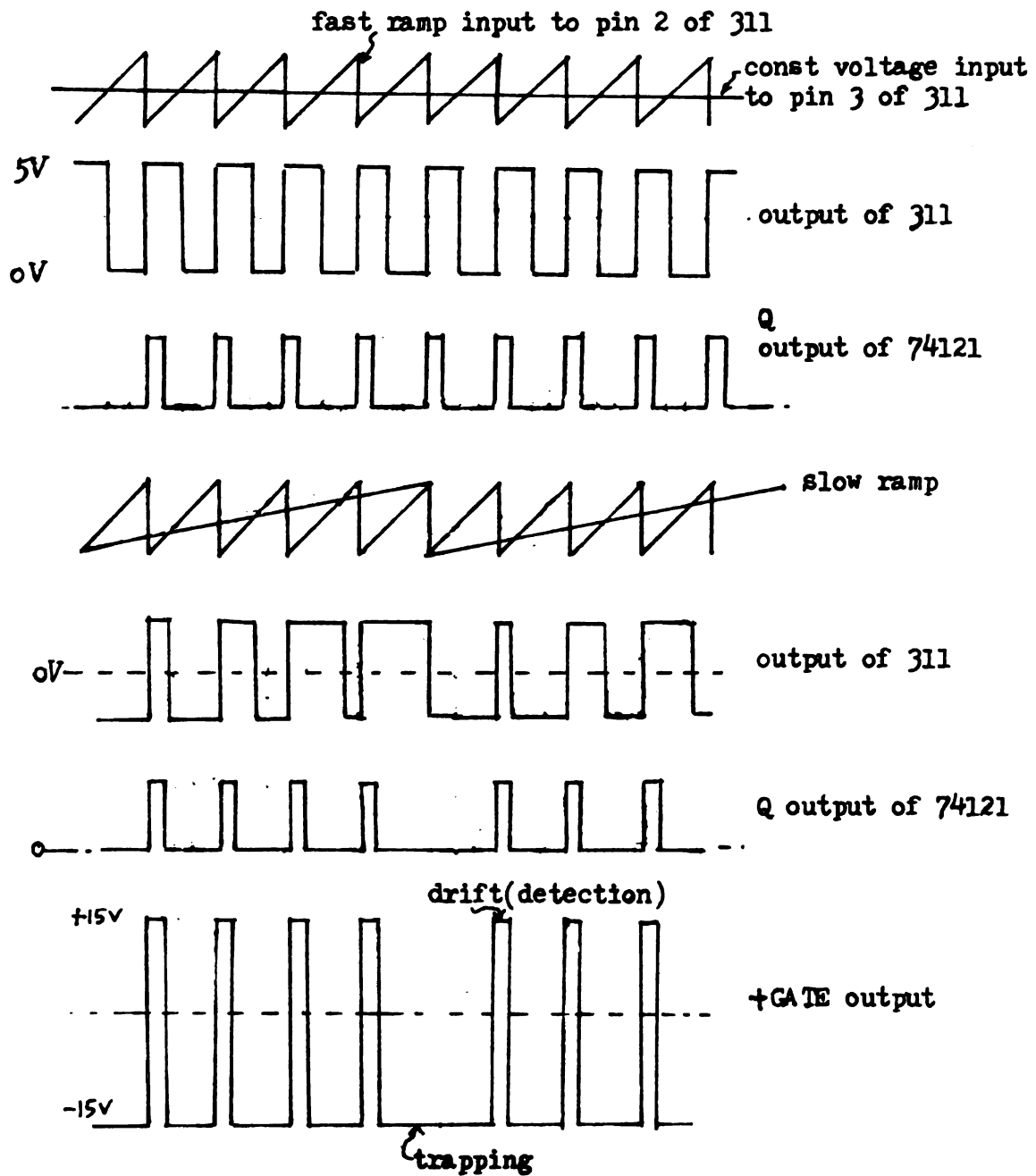
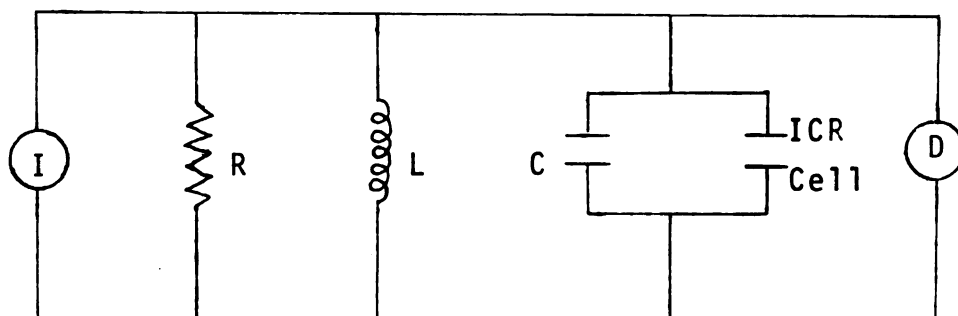


Figure 16. Timings Of Trapped Ion Cell Circuitry
In Figure 12

Appendix B.

Marginal Oscillator Setup In ICR Experiment

The tank circuit of a marginal oscillator is shown below:



The principle of detecting ions is in references 10 and 11.

APPENDIX C.

The Relationship Between Magnetic Field And Mass In The ICR Experiment

$$\omega_c = \frac{eB}{mc} = 2\pi\nu_c$$

$$\therefore B = \frac{\nu_c 2\pi m}{e}$$

At resonance, $\nu_c = \nu_{m.o}$

for $m = 100$ and if $\nu_{m.o} = 153 \text{ kHz}$

then

$$B = \frac{1.53 \times 10^5 \text{ Hz} \times 100 \text{ amu} \times 1.67 \times 10^{-27} \text{ kg/amu} \times 2\pi}{1.6 \times 10^{-19} \text{ coul}}$$

$$= 1.0028 \text{ W/m}^2 = 10028 \text{ G} = 10.028 \text{ kG}$$

Similarly,

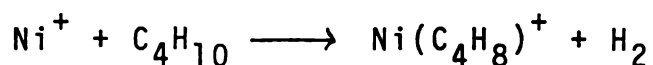
$$\text{for } m = 350, B = 3.510 \text{ W/m}^2 = 35.1 \text{ kG}$$

Therefore, by setting $\nu_{m.o} = 153 \text{ kHz}$, at 10 kG we can get a peak corresponding to m/e 100 and at 35 kG, we can get a peak corresponding mass unit of 350 amu.

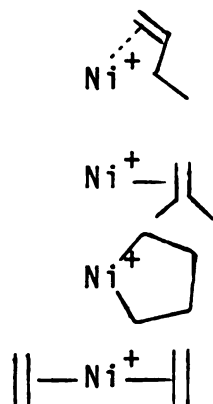
APPENDIX D.

Alternate CID Circuit For Conventional ICR

Double resonance techniques in ICR can be used to unambiguously identify the precursors of products. Yet, sometimes it is hard to determine the structure of product ions. For example,



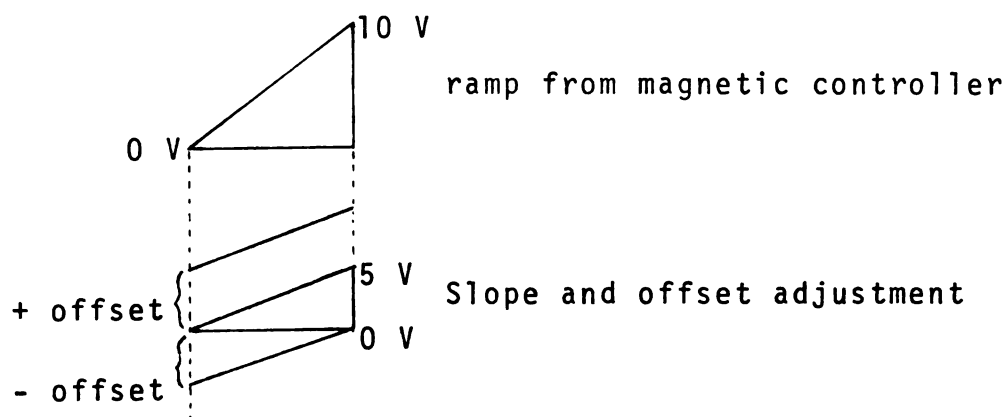
many possible structures can be assigned to $\text{Ni}(\text{C}_4\text{H}_8)^+$:



Substitution reactions can solve some of these questions. However, collisional-induced dissociation (CID)^{120,121} is a good technique for distinguishing one structure from another.

In conventional ICR, one can design a circuit which will excite or eject an ion while scanning the magnetic field. If that ion we are exciting is the product ion, it will gain energy from a radiofrequency (r.f.) and will actively collide

with neutral molecules and then dissociate. We also can excite any reactant ions to determine how kinetic energy imparted to them affects the reaction. Fig. 18 shows this design which was constructed. Note that a ramp (0-10v) from the magnet controller is fed into the op-amp to reduce the ramp to 0-5v, which is the useful range that can be fed into the VCG of a Wavetek frequency generator. In this way, the angular frequency of the ion will be linked with magnetic field while scanning the magnetic field. A 10 turn pot is used for slope adjustment. The circuit in the upper section is for offset about 5v as shown below



The fine adjustment offset value is done by use of a 500 k pot.

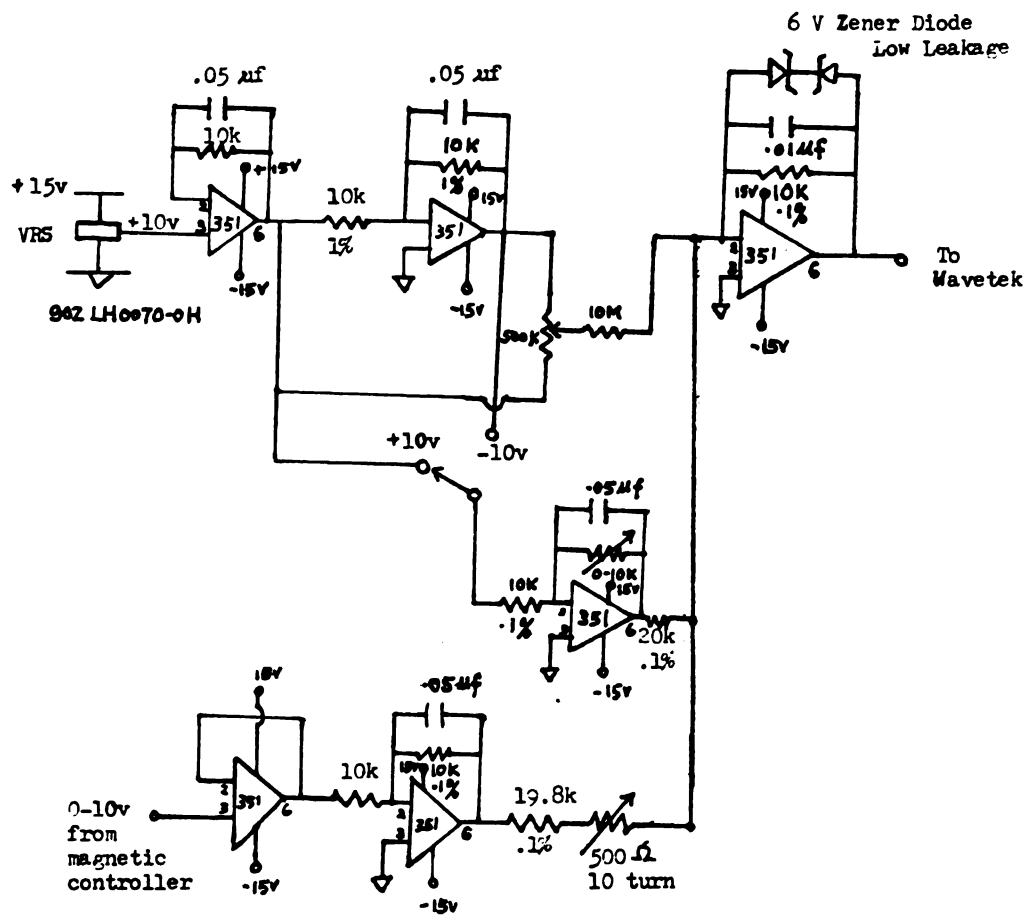


Figure 18. Schematic Circuit Diagram Of CID For Conventional ICR.

Appendix E.

Calculation Of The Collision Frequency For Co^+ And $\text{C}_4\text{H}_{10}\text{O}$

(1) polarizability¹⁶

$$\alpha (\text{ahc}) = \frac{4}{N} (\sum_A \tau_A)^2 A^3$$

where N is total electrons of molecule

α is polarizability

τ_A is atomic hybrid components obtained from Table I in Ref. 16.

$$\begin{aligned} \therefore \alpha_{\text{C}_4\text{H}_{10}\text{O}} &= \frac{4}{42} [(\tau_{\text{C}} + 3\tau_{\text{H}} + \tau_{\text{C}} + 2\tau_{\text{H}})_2 + \tau_{\text{O}}]^2 \\ &= \frac{4}{42} [(1.294 + 3 \times 0.314 + 1.294 + 2 \times 0.314)_2 + 1.290]^2 \\ &= \frac{4}{42} (92.275) = 8.7889 \text{ A}^3 \text{ expt'l} = 8.73 \text{ A}^3 \end{aligned}$$

(2) Langevin collision rate¹⁷

$$K_L = 2\pi e \left(\frac{\alpha}{\mu}\right)^{1/2} \text{ where } \mu \text{ is the reduced mass}$$

$$\therefore \mu = \frac{59 \times 90}{59 + 90} = 35.63758$$

$$\therefore K_L = 2 \times 3.14 \times 4.8 \times 10^{-10} \times \left(\frac{8.73 \times 10^{-24} \text{ cm}^3}{35.63758 \times 1.67 \times 10^{-24} \text{ g}} \right)^{1/2}$$

$$= 1.1545 \times 10^{-9} \text{ cm}^3/\text{molecules}$$

(3) collision frequency is $K_L \cdot N$

$$\text{But } \frac{N}{V} = \frac{P(\text{torr}) \times 6.02 \times 10^{23}}{760 \times 0.082 \times 298} = 3.24155 \times 10^{19} \text{ molecules/l}$$

$$\therefore N = P \times 3.24155 \times 10^{16} \text{ molecules/cm}^3 = 3.24155 \times 10^{16} \text{ molecules/cm}^3 \text{ at } 25^\circ\text{C}$$

at $P = 5 \times 10^{-6} \text{ torr}$ for ethyl ether

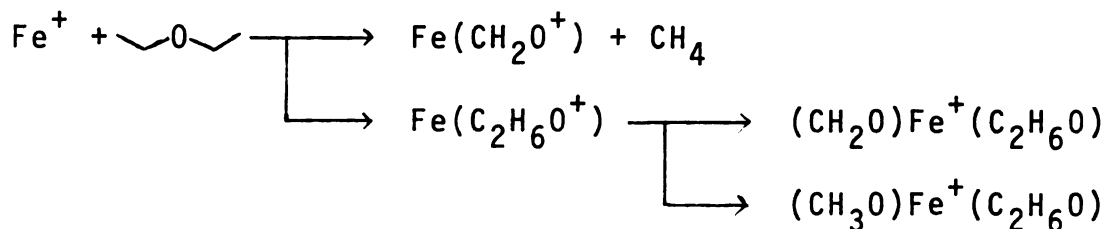
$$N = 5 \times 10^{-6} \times 3.24155 \times 10^{16} = 16.20775 \times 10^{10} \text{ molecules /cm}^3$$

$$\therefore \text{collision frequency} = K_L N = 1.1545 \times 10^{-9} \times 16.20775 \times 10^{10} = 187.11898 \text{ s}^{-1}$$

$$(4) \text{ time between collisions } \frac{1}{f} = \frac{1}{187.11898} = 5.34419 \times 10^{-3} \text{ s}$$

Appendix F.

Branching Ratios Of Fe^+ Reactions with —O—



The absolute intensity of each peak and the absolute power drop in the double resonance spectra are arbitrary but they have to be in the same scale.

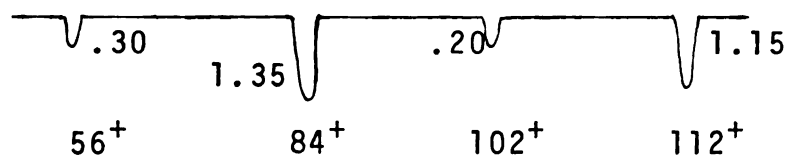
First, we have to take the peak height for each peak in question (m/e 86, 102, 132, and 133 in this case)

<u>m/e</u>	<u>ion</u>	<u>peak height</u>	<u>corrected peak height</u>
86	$\text{Fe}^+(\text{CH}_2\text{O})$	.80	9.30
102	$\text{Fe}^+(\text{C}_2\text{H}_6\text{O})$	2.75	27.0
132	$(\text{CH}_2\text{O})\text{Fe}^+(\text{C}_2\text{H}_6\text{O})$	.68	5.15
133	$(\text{CH}_3\text{O})\text{Fe}^+(\text{C}_2\text{H}_6\text{O})$	2.63	19.8

where corrected peak height = peak height/mass of the ion.

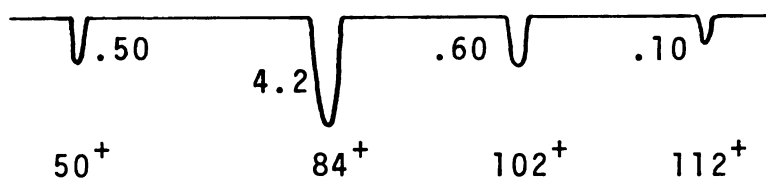
$$\text{Total } \text{Fe}^+(\text{C}_2\text{H}_6\text{O}) \text{ from } \text{Fe}^+ = I_{102^+} + I_{132^+} + I_{133^+}$$

Double resonance spectra of m/e 132



∴ % of m/z 132⁺ contribution from Fe(C₂H₆O)⁺ =

$$\frac{.20}{(.30+1.35+.20+1.15)} = .07$$

Double resonance spectra of m/3 133⁺

∴ % of m/e 133⁺ contribution from Fe⁺(C₂H₆O) =

$$\frac{.60}{(.50+4.2+.60+.10)} = .11$$

∴ total contribution of m/3 132⁺, 133⁺ from m/e 102⁺ is:

$$I_{132+}(.07) + I_{133+}(.11) = 5.15 \times .07 + 19.8 \times .11 =$$

$$.34 + 2.19 = 2.54$$

∴ branch ratio of m/e 132⁺ = .34/2.54 = .14

∴ branch ratio of m/e 133⁺ = 2.19/2.54 = .86

∴ total contribution of Fe⁺(C₂H₆O) from Fe⁺ = I₁₀₂₊ +

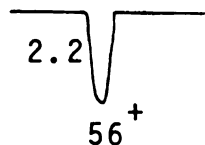
$$I_{132+} + I_{133+}$$

$$= 27.0 + (.07) \times I_{132+} + (.11) \times I_{133+}$$

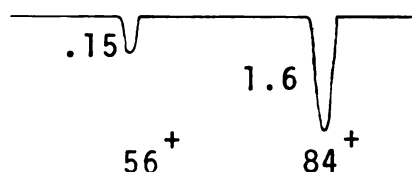
$$= 27.0 + .07 \times 5.15 + .11 \times 19.8$$

$$= 29.5$$

The double resonance spectra of m/e 86 appears as follows:



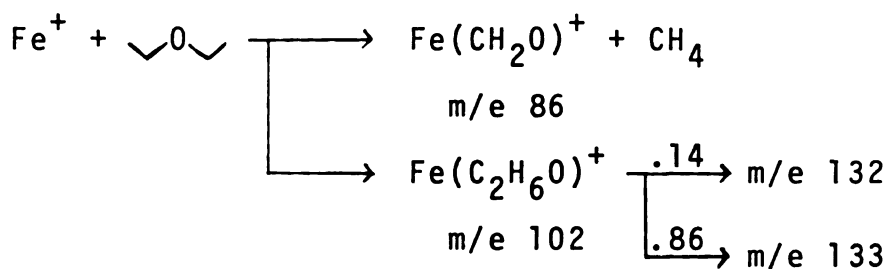
and m/e 102⁺:



$\therefore$ % contribution from Fe^+

$$= \frac{.15}{.15+1.6} = .09$$

m/e 132⁺, 133⁺ should be from successive reaction by m/e 102⁺ and m/e 86⁺



$$\text{Total contribution from } Fe^+ = I_{86^+} + (.09) \times I_{102^+}$$

$$= 9.302 + .09 \times 29.5 = 9.30 + 2.54$$

$$= 11.8$$

$$\therefore \text{ branching ratio of } m/e \ 86^+ = 9.3/11.8 = .79$$

$$\therefore \text{ branching ratio of } m/e \ 102^+ = 2.54/11.8 = .21$$

However, if we assume all m/e 132⁺, 133⁺ are from successive reaction of m/e 102⁺, then;

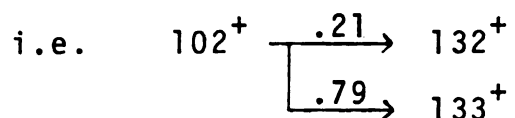
$$\begin{aligned}
 \text{Total } Fe^+(C_2H_6O) \text{ from } Fe^+ &= I_{102^+} + I_{132^+} + I_{133^+} = 27.0 \\
 &+ 5.15 + 19.8 = 51.9
 \end{aligned}$$

∴ % of m/e 132^+ contribution from $\text{Fe}^+(\text{C}_2\text{H}_6\text{O}) =$

$$5.15/(5.15 + 19.8) = .21$$

∴ % of m/e 133^+ contribution from $\text{Fe}^+(\text{C}_2\text{H}_6\text{O}) =$

$$19.77/(5.15 + 19.8) = .79$$

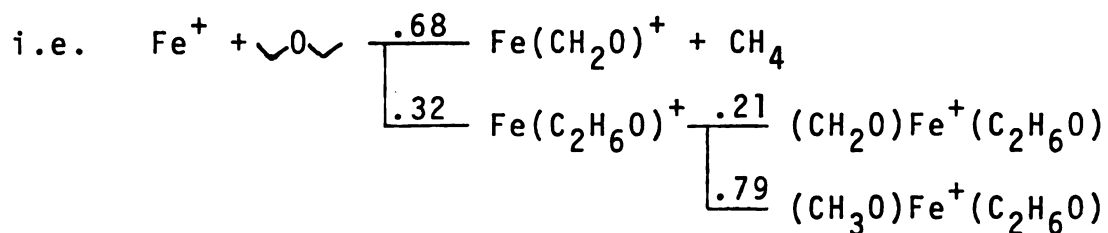


Total contribution from $\text{Fe}^+ = I_{86^+} + (.09)I_{102^+} = 9.30 +$

$$(.09) \times 51.9 = 13.8$$

∴ branching ratio of $86^+ = 9.30/13.8 = .68$

∴ branching ratio of $102^+ = 4.46/13.8 = .32$



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