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Organometallics, 1983, 2 (7), 883-890 • DOI: 10.1021/om50001a018 • Publication Date (Web): 01 May 2002

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Gas-Phase Chemistry of Univalent Transition-Metal and Metal-Containing Ions with Polyethers: Triethylene Glycol Dimethyl Ether and Its Cyclic Analogue 12-Crown-4

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Received December 7, 1982

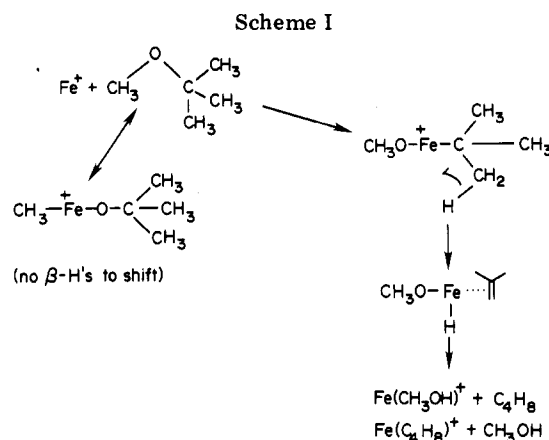
The mechanisms through which a number of metal and metal-containing ions react with gaseous monofunctional organic molecules have appeared in the literature. We report here mechanisms through which chromium and iron ions and complexes of these ions react with highly functionalized molecules—polyethers. Cyclic polyethers react much differently with gas-phase metal ions than their straight-chain analogues. Mechanisms operable for reactions with diethyl ether also hold for linear polyethers. Such mechanisms are not operable for cyclic compounds, although variations on the commonly used metal insertion, β -H shift mechanism can be used. The differences in the chemistry of Cr^+ and Fe^+ can be interpreted in terms of strong Cr^+ -O interactions.

Introduction

Studies of the interaction of metal ions with large ligands such as crown ethers and cryptands *in solution* have been informative in elucidating the dynamics of ion-solvent interactions.¹ The body of literature involving mass spectrometric studies of *gas-phase* ion-molecule reactions has provided novel insights into the bimolecular chemistry of ions with neutral molecules in the *absence* of complicating solvent phenomena.² While such gas-phase experiments should be very complimentary to solution studies and should allow the determination of the *role* of solvent in solution, such actual correlation work is rare.^{3,4}

In the past several years, a body of literature has grown involving the gas-phase chemistry of metal and metal-containing ions with neutral organic molecules, i.e., gas-phase organometallic chemistry. Most of these studies are concerned with ligand-free univalent metal ions (such as Fe^+ , Al^+ , Co^+ , Li^+) with molecules containing either one functional group (such as alcohols, alkyl halides, ethers, amines) or no functional groups (alkanes).⁵ Recently, metal ion reactions with multifunctional organic molecules have also been reported.⁶

This paper discusses the gas-phase chemistry of $\text{Cr}(\text{CO})_n^+$ ($n = 0-6$) and $\text{Fe}(\text{CO})_n^+$ ($n = 0-5$) with diethyl ether and two polyethers, 12-crown-4 (12-C-4) and triethylene glycol dimethyl ether (TDE), as studied by ion cyclotron resonance (ICR) spectrometry.⁷ The original goal of this work was to form metal ion-crown complexes in the gas phase and compare the chemistry of M^+ to that of $\text{M}^+(\text{crown})$ with simple molecules such as alkyl halides (since that chemistry for M^+ alone is well understood). Instead, we discovered that metal ion-crown ether complexes are not simple to make in the gas phase because,



on complexation with a metal ion, a large amount of energy is released and extensive fragmentation of the crown ether is observed. The products of these reactions give useful insights into the interaction of gaseous metal ions with polyethers. The chemistry of metal ions with cyclic polyethers is much richer than with linear polyethers. This will be explained as a "mechanistic" macrocyclic effect.⁸

Univalent gaseous metal ions react with simple ethers by fairly well understood mechanisms. The chemistry of ions of the type TiCl_n^+ ($n = 0-4$) with some simple aliphatic ethers has been reported by Allison and Ridge.⁹ Of more direct interest to this work is the study of the gas-phase chemistry of Fe^+ with a number of ethers by Freiser *et al.*¹⁰ They report that Fe^+ reacts with ethers through a frequently used mechanism of metal insertion into the polar (C-O) bond, followed by a shift of a hydrogen atom which is on a carbon atom which is β to the metal.¹¹ Thus, in the case of methyl isobutyl ether, the metal can presumably insert into either C-O bond, but no products appear to be formed following Fe^+ insertion into the

(1) See, for example: Popov, A. I. *Pure Appl. Chem.* 1979, 51, 101.

(2) See, for example: Bowers, M. T., Ed. "Gas Phase Ion Chemistry"; Academic Press: New York, 1979; Vols. 1 and 2.

(3) Bohme, D. K.; Rakshit, A. B.; Mackay, G. I. *J. Am. Chem. Soc.* 1982, 104, 1100.

(4) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* 1975, 98, 318.

(5) Publications representative of the groups active in this area include: (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1980, 102, 1736. (b) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* 1980, 52, 164. Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* 1979, 101, 1332. Uppal, J. S.; Staley, R. H. *Ibid.* 1980, 102, 3794.

(6) Lombarski, M.; Allison, J. *Int. J. Mass Spectrom. Ion Phys.* 1983, 49, 281.

(7) For a review of ICR: Lehman, T. A.; Bursley, M. M. "Ion Cyclotron Resonance Spectrometry"; Wiley-Interscience: New York, 1976.

(8) This term was first used in a communication by: Huang, S.; Lee, Y. C.; Popov, A. I.; Allison, J., accepted for publication in *Spectrosc. Lett.*

(9) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* 1978, 100, 163.

(10) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* 1981, 103, 4360. In this work, it is reported that Fe^+ reacts with diethyl ether to form four products resulting in elimination of $\text{C}_2\text{H}_6\text{O}$, C_2H_6 , C_2H_4 , and H_2 in relative amounts of 0.23:0.23:0.47:0.07. This compares well with our branching ratios of 0.33:0.24:0.41:0.02.

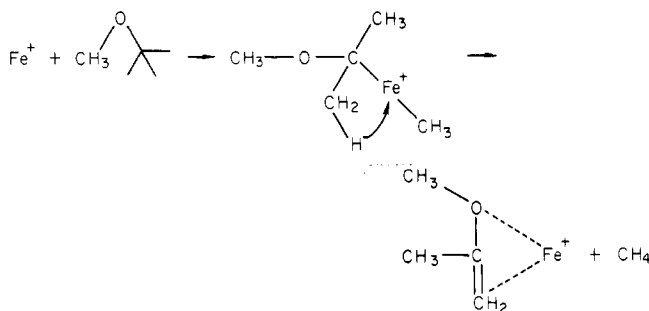
(11) This mechanism was first confirmed not for ethers but for other polar organic molecules such as alkyl halides and alcohols in: Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* 1976, 98, 7445.

Table I. Reactions of $M(\text{CO})_x^+$ with Diethyl Ether ($\text{C}_4\text{H}_{10}\text{O}$)

reaction	x	
	M = Fe	M = Cr
$M(\text{CO})_x^+ + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow M(\text{CO})_x\text{C}_2\text{H}_4\text{O}^+ + \text{C}_2\text{H}_6$	0	0
$\rightarrow M(\text{CO})_x\text{C}_2\text{H}_6\text{O}^+ + \text{C}_2\text{H}_4$	0	
$\rightarrow M(\text{CO})_x\text{C}_2\text{H}_4^+ + \text{C}_2\text{H}_6\text{O}$	0	
$\rightarrow M(\text{CO})_x\text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_4\text{O}$		1
$\rightarrow M(\text{CO})_x\text{C}_4\text{H}_8\text{O}^+ + \text{H}_2$	0	
$\rightarrow M(\text{CO})_{x-1}\text{C}_4\text{H}_{10}\text{O}^+ + \text{CO}$	1, 2, 4, 5	1, 2, 5
$\rightarrow M(\text{CO})_{x-2}\text{C}_4\text{H}_{10}\text{O}^+ + 2\text{CO}$	2, 4, 5	2, 3
$\rightarrow M(\text{CO})_{x-1}\text{C}_2\text{H}_4\text{O}^+ + \text{C}_2\text{H}_6 + \text{CO}$	1	
$\rightarrow M(\text{CO})_{x-1}\text{C}_2\text{H}_6\text{O}^+ + \text{C}_2\text{H}_4 + \text{CO}$	1	
$\rightarrow M(\text{CO})_{x-2}\text{C}_2\text{H}_6\text{O}^+ + \text{C}_2\text{H}_4 + 2\text{CO}$	2	
$\rightarrow M(\text{CO})_{x-1}\text{C}_4\text{H}_8\text{O}^+ + \text{H}_2 + \text{CO}$	1	
$\rightarrow M(\text{CO})_{x-3}\text{C}_4\text{H}_{10}\text{O}^+ + 3\text{CO}$	3, 4	

$\text{CH}_3\text{-O}$ bond due to the absence of a $\beta\text{-H}$ atom in the intermediate (Scheme I).¹⁰

Also, the product $\text{FeC}_4\text{H}_8\text{O}^+$ was observed, corresponding to elimination of methane. This product and others observed by Freiser can be explained by insertion of Fe^+ into a C-C bond:



That is, the major products apparently follow Fe^+ insertion into C-O with minor products being formed from C-C insertion mechanisms. This seems reasonable since, although the initial interaction of Fe^+ is with a lone pair on the oxygen, Fe^+ -alkyl bonds are strong and may favor insertion into a carbon-carbon bond.¹²

Here, the chemistry of Cr^+ , Fe^+ , and ions of the type $M(\text{CO})_x^+$ with diethyl ether will be reported to indicate the behavior of these metal ions (note—Freiser et al.¹⁰ previously reported the chemistry of Fe^+ with diethyl ether) with simple ethers. The reaction mechanisms will provide a framework for interpreting the results of the metal center reactions with the polyethers.

Experimental Section

The experiments described here were performed on an ion cyclotron resonance spectrometer (used in the "drift" mode) of conventional design which has been described elsewhere.¹³ Spectra of 1:1 (metal carbonyl/ether) mixtures at total pressures up to 1×10^{-5} torr were taken up to at least m/z 300, reaction products identified, and their precursors determined by using conventional double resonance techniques. $\text{Fe}(\text{CO})_5$, TDE, and 12-crown-4 were obtained from Aldrich Chemical Co. $\text{Cr}(\text{CO})_6$ was obtained from Alfa Products. Diethyl ether was obtained from Mallinckrodt, Inc. Diethyl ether and TDE were refluxed with excess Na metal for 12 h and then vacuum distilled under N_2 to remove H_2O . All compounds were subjected to standard freeze-pump-thaw cycles before use.

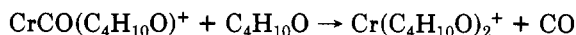
Results

The ion/molecule reactions observed for the $\text{Cr}(\text{CO})_n^+$ and $\text{Fe}(\text{CO})_n^+$ ions with diethyl ether are presented in

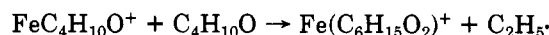
(12) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1981, 103, 6501.

(13) Radecki, B.; Allison, J., submitted for publication in *J. Am. Chem. Soc.*

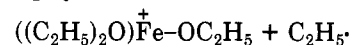
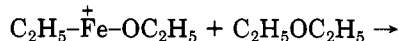
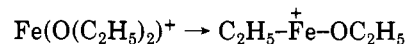
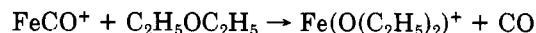
Table I. Subsequent reactions of the product ions of Table I are observed, e.g.



but will not be discussed. In the case of the $\text{Fe}(\text{CO})_5^-$ -diethyl ether mixture, an interesting subsequent reaction was observed for $\text{FeC}_4\text{H}_{10}\text{O}^+$:



This may be an indication that diethyl ether exists on Fe^+ not as the intact ether but as two σ -bonded groups, C_2H_5^- and $\text{C}_2\text{H}_5\text{O}^-$, that is



All of the ethers which were used in this work contained small amounts of water. In the case of diethyl ether, since the mass spectrum is known, the presence of water could be detected. In the case of TDE and 12-crown-4, compounds whose mass spectra have not been adequately reported,¹⁴ the presence/absence of H_2O was less clear. Thus, on occasions when water-containing products were observed, it was unclear whether the reactions were H_2O displacement of CO or removal of H_2O from the ether by the metal ion. Because of this, these few questionable products will not be reported.

Tables II-V list the observed reaction products in the metal carbonyl-polyether mixtures. The m/z of a product ion and its precursors are listed. An assignment of the composition of each product ion is proposed. In these experiments, a few product ions cannot be unambiguously assigned because of the C_2H_4 vs. CO mass problem (both correspond to 28 u). The proposed assignments were chosen on the basis of a number of criteria, mainly reasonability and internal consistency. For example, in Table II, m/z 110 corresponds to Cr^+ with a ligand containing 58 u. A mass of 58 could be C_4H_{10} , $\text{C}_3\text{H}_6\text{O}$, or $\text{C}_2\text{H}_2\text{O}_2$. Based on what is known about such gas-phase processes and based on the structure of the reactant molecule TDE, we chose $\text{C}_3\text{H}_6\text{O}$ as being the most reasonable grouping of atoms with a mass of 58 u. Thus, we assign m/z 110 to

(14) A paper detailing the mass spectra of the series of crown ethers, 12-crown-4, 15-crown-5, 18-crown-6, and 21-crown-7, has been accepted for publication: Lee, Y. C.; Popov, A. I.; Allison, J. *Int. J. Mass Spectrom. Ion Phys.*, in press.

(15) This is also observed on electron impact—see, e.g., Whitney, R. R.; Jaeger, D. A. *Org. Mass Spectrom.* 1980, 15, 343.

(16) Based on the $\Delta H_f^\circ(12\text{-C-4}) = -150.8$ kcal/mol as per Bystrom, K.; Mansson, M. *J. Chem. Soc., Perkin Trans. 2* 1982, 566 and $\Delta H_f^\circ(1,4\text{-dioxane}) = -85$ kcal/mol as per ref 17.

Table II. Ion-Molecule Reaction Products of $\text{Cr}(\text{CO})_x^+$ Ions with Triethylene Glycol Dimethyl Ether ($\text{C}_8\text{H}_{18}\text{O}_4$)

product m/z	assign	precursors	corresponding neutral products
84	CrCH_3O^+	CrCO^+	$\text{C}_7\text{H}_{14}\text{O}_3 + \text{CO}$
		$\text{Cr}(\text{CO})_2^+$	$\text{C}_7\text{H}_{14}\text{O}_3 + 2\text{CO}$
96	$\text{CrC}_2\text{H}_4\text{O}^+$	Cr^+	$\text{C}_6\text{H}_{14}\text{O}_3$
110	$\text{CrC}_3\text{H}_6\text{O}^+$	CrCO^+	$\text{C}_5\text{H}_{12}\text{O}_3 + \text{CO}$
		$\text{Cr}(\text{CO})_2^+$	$\text{C}_5\text{H}_{12}\text{O}_3 + 2\text{CO}$
112	$\text{CrCO}(\text{CH}_4\text{O})^+$	CrCO^+	$\text{C}_7\text{H}_{14}\text{O}_3$
		$\text{Cr}(\text{CO})_2^+$	$\text{C}_7\text{H}_{14}\text{O}_3 + \text{CO}$
126	$\text{CrC}_3\text{H}_6\text{O}_2^+$	Cr^+	$\text{C}_5\text{H}_{12}\text{O}_2$
		CrCO^+	$\text{C}_5\text{H}_{12}\text{O}_2 + \text{CO}$
		$\text{Cr}(\text{CO})_2^+$	$\text{C}_5\text{H}_{12}\text{O}_2 + 2\text{CO}$
128	$\text{CrC}_3\text{H}_8\text{O}_2^+$	Cr^+	$\text{C}_5\text{H}_{10}\text{O}_2$
		CrCO^+	$\text{C}_5\text{H}_{10}\text{O}_2 + \text{CO}$
		$\text{Cr}(\text{CO})_2^+$	$\text{C}_5\text{H}_{10}\text{O}_2 + 2\text{CO}$
138	$\text{Cr}(\text{CO})\text{C}_3\text{H}_6\text{O}^+$	$\text{Cr}(\text{CO})_2^+$	$\text{C}_5\text{H}_{12}\text{O}_3 + \text{CO}$
		$\text{Cr}(\text{CO})_3^+$	$\text{C}_5\text{H}_{12}\text{O}_3 + 2\text{CO}$
140	$\text{Cr}(\text{CO})_2\text{CH}_4\text{O}^+$	$\text{Cr}(\text{CO})_2^+$	$\text{C}_7\text{H}_{14}\text{O}_3$
		$\text{Cr}(\text{CO})_3^+$	$\text{C}_7\text{H}_{14}\text{O}_3 + \text{CO}$
142	$\text{CrC}_4\text{H}_{10}\text{O}_2^+$	CrCO^+	$\text{C}_4\text{H}_8\text{O}_2 + \text{CO}$
		$\text{Cr}(\text{CO})_2^+$	$\text{C}_4\text{H}_8\text{O}_2 + 2\text{CO}$
156	$\text{Cr}(\text{CO})\text{C}_3\text{H}_8\text{O}_2^+$	CrCO^+	$\text{C}_5\text{H}_{10}\text{O}_2$
		$\text{Cr}(\text{CO})_2^+$	$\text{C}_5\text{H}_{10}\text{O}_2 + \text{CO}$
166	$\text{Cr}(\text{CO})_2\text{C}_3\text{H}_6\text{O}^+$	$\text{Cr}(\text{CO})_2^+$	$\text{C}_5\text{H}_{12}\text{O}_3$
168	$\text{Cr}(\text{CO})\text{C}_4\text{H}_8\text{O}_2^+$	CrCO^+	$\text{C}_4\text{H}_8\text{O}_2$
		$\text{Cr}(\text{CO})_2^+$	$\text{C}_4\text{H}_8\text{O}_2 + \text{CO}$
170	$\text{Cr}(\text{CO})\text{C}_4\text{H}_{10}\text{O}_2^+$	CrCO^+	$\text{C}_4\text{H}_8\text{O}_2$
		$\text{Cr}(\text{CO})_2^+$	$\text{C}_4\text{H}_8\text{O}_2 + \text{CO}$

Table III. Ion-Molecule Reaction Products of $\text{Fe}(\text{CO})_x^+$ Ions with Triethylene Glycol Dimethyl Ether ($\text{C}_8\text{H}_{18}\text{O}_4$)

product m/z	assign	precursors	corresponding neutral products
114	$\text{FeC}_3\text{H}_6\text{O}^+$	Fe^+	$\text{C}_5\text{H}_{12}\text{O}_3$
		FeCO^+	$\text{C}_5\text{H}_{12}\text{O}_3 + \text{CO}$
116	$\text{Fe}(\text{CO})\text{CH}_4\text{O}^+$	FeCO^+	$\text{C}_7\text{H}_{14}\text{O}_3$
		$\text{Fe}(\text{CO})_2^+$	$\text{C}_7\text{H}_{14}\text{O}_3 + \text{CO}$
132	$\text{FeC}_3\text{H}_8\text{O}_2^+$	$\text{Fe}(\text{CO})_2^+$	$\text{C}_5\text{H}_{10}\text{O}_2 + 2\text{CO}$
		$\text{Fe}(\text{CO})_3^+$	$\text{C}_5\text{H}_{10}\text{O}_2 + 3\text{CO}$
142	$\text{FeCOC}_3\text{H}_6\text{O}^+$	$\text{Fe}(\text{CO})_2^+$	$\text{C}_5\text{H}_{12}\text{O}_3 + \text{CO}$
144	$\text{FeCOC}_3\text{H}_8\text{O}^+$	$\text{Fe}(\text{CO})_2^+$	$\text{C}_5\text{H}_{10}\text{O}_3 + \text{CO}$
		$\text{Fe}(\text{CO})_3^+$	$\text{C}_5\text{H}_{10}\text{O}_3 + 2\text{CO}$
158	$\text{FeCOC}_3\text{H}_6\text{O}_2^+$	$\text{Fe}(\text{CO})_4^+$	$\text{C}_5\text{H}_{10}\text{O}_2 + \text{H}_2 + 3\text{CO}$
160	$\text{FeCOC}_3\text{H}_8\text{O}_2^+$	$\text{Fe}(\text{CO})_4^+$	$\text{C}_5\text{H}_{10}\text{O}_2 + 3\text{CO}$
170	$\text{Fe}(\text{CO})_2\text{C}_3\text{H}_6\text{O}^+$	$\text{Fe}(\text{CO})_2^+$	$\text{C}_5\text{H}_{12}\text{O}_3$
172	$\text{Fe}(\text{CO})\text{C}_4\text{H}_8\text{O}_2^+$	FeCO^+	$\text{C}_4\text{H}_8\text{O}_2$
		$\text{Fe}(\text{CO})_2^+$	$\text{C}_4\text{H}_8\text{O}_2 + \text{CO}$
		$\text{Fe}(\text{CO})_3^+$	$\text{C}_4\text{H}_8\text{O}_2 + 2\text{CO}$
188	$\text{Fe}(\text{CO})_2\text{C}_3\text{H}_8\text{O}_2^+$	$\text{Fe}(\text{CO})_3^+$	$\text{C}_5\text{H}_{10}\text{O}_2 + \text{CO}$
		$\text{Fe}(\text{CO})_4^+$	$\text{C}_5\text{H}_{10}\text{O}_2 + 2\text{CO}$
		$\text{Fe}(\text{CO})_5^+$	$\text{C}_5\text{H}_{10}\text{O}_2 + 3\text{CO}$
202	$\text{Fe}(\text{CO})_2\text{C}_4\text{H}_{10}\text{O}_2^+$	$\text{Fe}(\text{CO})_2^+$	$\text{C}_4\text{H}_8\text{O}_2$
		$\text{Fe}(\text{CO})_3^+$	$\text{C}_4\text{H}_8\text{O}_2 + \text{CO}$
		$\text{Fe}(\text{CO})_4^+$	$\text{C}_4\text{H}_8\text{O}_2 + 2\text{CO}$

Table IV. Ion-Molecule Reaction Products of $\text{Cr}(\text{CO})_x^+$ Ions with 12-Crown-4 ($\text{C}_8\text{H}_{16}\text{O}_4$)

product m/z	assign	precursors	corresponding neutral products
96	$\text{CrC}_2\text{H}_4\text{O}^+$	Cr^+	$\text{C}_6\text{H}_{12}\text{O}_3$
112	$\text{CrC}_2\text{H}_4\text{O}_2^+$	Cr^+	$\text{C}_6\text{H}_{12}\text{O}_2$
128	$\text{CrC}_2\text{H}_4\text{O}_3^+$	Cr^+	$\text{C}_2\text{H}_4 + \text{C}_4\text{H}_8\text{O}$
156	$\text{CrC}_4\text{H}_8\text{O}_3^+$	Cr^+	$\text{C}_4\text{H}_8\text{O}$
		CrCO^+	$\text{C}_4\text{H}_8\text{O} + \text{CO}$
		$\text{Cr}(\text{CO})_2^+$	$\text{C}_4\text{H}_8\text{O} + 2\text{CO}$
200	$\text{CrC}_6\text{H}_{12}\text{O}_4^+$	Cr^+	C_2H_4
		CrCO^+	$\text{C}_2\text{H}_4 + \text{CO}$
		$\text{Cr}(\text{CO})_2^+$	$\text{C}_2\text{H}_4 + 2\text{CO}$
228	$\text{CrC}_8\text{H}_{16}\text{O}_4^+$	CrCO^+	CO
		$\text{Cr}(\text{CO})_2^+$	2CO

be $\text{CrC}_3\text{H}_6\text{O}^+$. Using such reasoning, mass 138 could be assigned the composition $\text{CrC}_5\text{H}_{10}\text{O}^+$. However, in order

Table V. Ion-Molecule Reaction Products of $\text{Fe}(\text{CO})_x^+$ Ions with 12-Crown-4 ($\text{C}_8\text{H}_{16}\text{O}_4$)

product m/z	assign	precursors	corresponding neutral products
98	$\text{FeC}_2\text{H}_2\text{O}^+$	Fe^+	$\text{C}_6\text{H}_{12}\text{O}_3 + \text{H}_2$
		FeCO^+	$\text{C}_6\text{H}_{12}\text{O}_3 + \text{H}_2 + \text{CO}$
114	$\text{FeC}_2\text{H}_2\text{O}_2$	Fe^+	$\text{C}_6\text{H}_{14}\text{O}_2$
		FeCO^+	$\text{C}_6\text{H}_{14}\text{O}_2 + \text{CO}$
116	$\text{FeC}_3\text{H}_8\text{O}^+$	Fe^+	$\text{C}_5\text{H}_8\text{O}_3$
124	$\text{FeC}_4\text{H}_8\text{O}^+$	Fe^+	$\text{C}_4\text{H}_{12}\text{O}_3$
126	$\text{FeC}_4\text{H}_6\text{O}^+$	Fe^+	$\text{C}_4\text{H}_{10}\text{O}_3$
		FeCO^+	$\text{C}_4\text{H}_6\text{O}_3 + \text{CO}$
130	$\text{FeC}_4\text{H}_{10}\text{O}^+$	Fe^+	$\text{C}_4\text{H}_6\text{O}_3$ or $\text{C}_5\text{H}_{10}\text{O}_2$
	or $\text{FeC}_2\text{H}_6\text{O}_2^+$	Fe^+	$\text{C}_5\text{H}_{10}\text{O}_3 + \text{CO}$
142	$\text{FeCOC}_3\text{H}_6\text{O}^+$	$\text{Fe}(\text{CO})_2^+$	$\text{C}_5\text{H}_{10}\text{O}_3 + \text{CO}$
144	$\text{FeC}_4\text{H}_8\text{O}_2^+$	Fe^+	$\text{C}_4\text{H}_8\text{O}_2$
		FeCO^+	$\text{C}_4\text{H}_8\text{O}_2 + \text{CO}$
160	$\text{FeC}_4\text{H}_8\text{O}_3^+$	Fe^+	$\text{C}_4\text{H}_8\text{O}$
		FeCO^+	$\text{C}_4\text{H}_8\text{O} + \text{CO}$
174	$\text{FeC}_6\text{H}_{14}\text{O}_2^+$	Fe^+	$\text{C}_2\text{H}_2\text{O}_2$
		FeCO^+	$\text{C}_2\text{H}_2\text{O} + \text{CO}$
204	$\text{FeC}_6\text{H}_{12}\text{O}_4^+$	FeCO^+	$\text{C}_2\text{H}_4 + \text{CO}$
		$\text{Fe}(\text{CO})_2^+$	$\text{C}_2\text{H}_4 + 2\text{CO}$

to minimize the number of reactions and by considering the precursors, mass 138, which is 28 mass units above 110, was considered to be m/z 110 + CO, or $\text{Cr}(\text{CO})(\text{C}_3\text{H}_6\text{O})^+$. Thus, by considering the structure of the species involved and cross-correlating reactants and products, we present what we feel to be accurate assignments for the products observed. (Deuterated polyethers would certainly be helpful in confirming these assignments.)

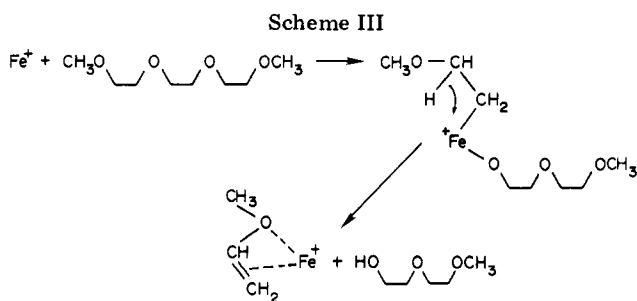
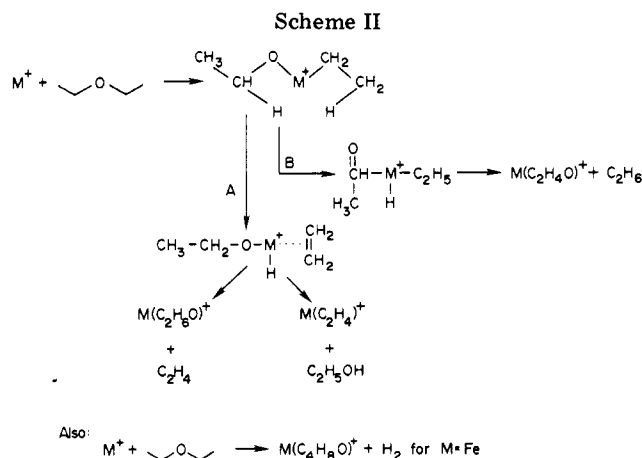
In almost all cases, when a metal center attacks an ether or polyether, the fragment retained by the metal corresponds (in u) to a simple fragment of the molecule ± 1 u for linear compounds and ± 2 u for cyclic reactants. Thus, extensive rearrangement of the skeletal atoms of the molecule does not appear to occur, greatly simplifying the product ion composition assignments.

Discussion

A. The Chemistry of Cr^+ and Fe^+ with Ethers and Polyethers. These two metals were chosen because of the possibility that they may exhibit contrasting reactivities with alkyl ethers from a thermodynamic standpoint. For Cr^+ , the bond strength to an oxygen atom is much greater than to an alkyl group such as CH_3 ($D(\text{Cr}^+-\text{O}) = 77 \pm 5$ kcal/mol; $D(\text{Cr}^+-\text{CH}_3) = 37 \pm 7$ kcal/mol).¹² In contrast, the interactions of Fe^+ with O and CH_3 are comparable ($D(\text{Fe}^+-\text{O}) = 68 \pm 3$ kcal/mol; $D(\text{Fe}^+-\text{CH}_3) = 68 \pm 4$ kcal/mol).¹² Indeed, we see reactions that appear to be dominated by the strong M^+-O interaction for Cr^+ which are not observed for Fe^+ .

1. Diethyl Ether. Cr^+ forms one product with diethyl ether and Fe^+ forms four. All products can be explained by using the metal insertion, β -H atom shift mechanism.¹¹ Scheme II shows that, if M^+ inserts into the C-O bond in diethyl ether, there are two different types of β -H atoms. If the H atom on the carbon which is β to the metal in the ethyl ligand shifts (pathway A), the $\text{M}(\text{C}_2\text{H}_6\text{O})^+$ and $\text{M}(\text{C}_2\text{H}_4)^+$ products are formed. If the β -H atom in the ethoxy group shifts, pathway B leads to $\text{M}(\text{C}_2\text{H}_4\text{O})^+$. Fe^+ reacts by pathways A and B and Cr^+ reacts by B only. The reason for this difference may be in part thermodynamic. Pathways A and B involve the reorganization of diethyl ether into two sets of products, (1) and (2). Cr^+ can induce the rearrangement (1) which requires very little energy, $\Delta H(1) = 0.30$ kcal/mol.¹⁷





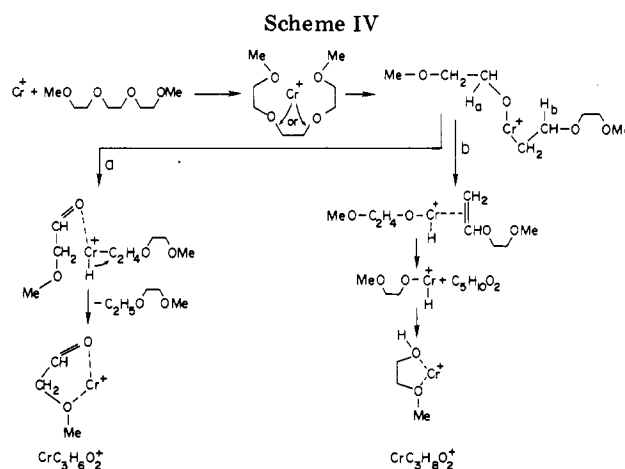
Fe^+ induces both rearrangements. More energy is required for process 2, $\Delta H(2) = 16.8$ kcal/mol. Thus Fe^+ forms "higher energy" products than does Cr^+ . This implies that the energy made available on initial complexation of M^+ and Et_2O is greater for Fe^+ than Cr^+ . This is consistent with the observation that diethyl ether will displace up to two CO's from Cr^+ and up to three CO's from Fe^+ (implying that the initial Cr^+ -ether interaction energy, 66.2 kcal/mol $< D(\text{Cr}^+-\text{Et}_2\text{O}) < 87.7$ kcal/mol, is less than that for Fe^+ , 96.6 kcal/mol $< D(\text{Fe}^+-\text{Et}_2\text{O}) < 133.3$ kcal/mol).^{17,25}

Thus, Cr^+ and Fe^+ react with diethyl ether by established mechanisms.

2. Triethylene Glycol Dimethyl Ether (TDE).

When the reactant neutral becomes a polyether, multiple metal-ligand interactions are expected, since these are observed in solution. Fe^+ forms one product with TDE, Cr^+ forms three, and the products are reasonable in terms of the same mechanism used for diethyl ether. 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).

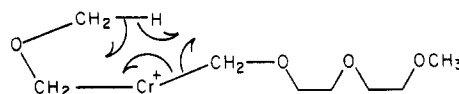
Fe^+ reacts with TDE to form $\text{FeC}_3\text{H}_6\text{O}^+$. Scheme III shows the implied mechanism. This mechanism is typical in that, when the metal ion rearranges TDE into two smaller molecules, the smaller one is usually retained as a ligand. The Fe^+ product, then, follows insertion into the bond between skeletal atoms 4 and 5. Cr^+ , by contrast, forms two products following insertion into the bond between skeletal atoms 5 and 6, $\text{CrC}_3\text{H}_6\text{O}_2^+$ and $\text{CrC}_3\text{H}_8\text{O}_2^+$. Attack of a more centrally located bond in the polyether



may be evidence for a symmetric intermediate involving multiple metal-ligand interaction, which is shown as the first step in Scheme IV.

Also, the strong Cr^+-O interaction may favor the formation of small ligands with more oxygens than does Fe^+ —explaining the difference in site of attack for Fe^+ and Cr^+ . Scheme IV shows the proposed mechanism for the formation of $\text{CrC}_3\text{H}_6\text{O}_2^+$ and $\text{CrC}_3\text{H}_8\text{O}_2^+$ from TDE. Again, there are two possible β -H atoms which can shift, and products due to each shift are observed. The smaller rearrangement product is again maintained by the metal and the larger product lost. Schemes III and IV both proceed via intermediates in which there are two different β -H atoms accessible to the metal. In Scheme III, products from only one shift are observed, while in Scheme IV, both types of products are observed. The favorability of such a H shift depends on the stability of the final product. Both pathways in Scheme IV form ligands that can donate four electrons to the electron-deficient metal. In Scheme III the β -H which is shown to shift forms a four-electron-donating ligand in the product. If a β -H atom shifted from the right side of the intermediate in Scheme III and the smaller ligand retained, it would be a two-electron donor. Thus, the option of which β -H's will shift is related in part to the ability of the final retained fragment product to be a good ligand.

Cr^+ also reacts with TDE to form $\text{CrC}_3\text{H}_4\text{O}^+$. 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 two carbons and one oxygen, 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



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

TDE, then, appears to react via the same mechanism as diethyl ether. 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.

3. 12-Crown-4. The chemistry of Cr^+ and Fe^+ with 12-crown-4 is much richer than that observed for the straight chain analogue. Fe^+ forms nine products with 12-crown-4; Cr^+ forms four products. The reaction prod-

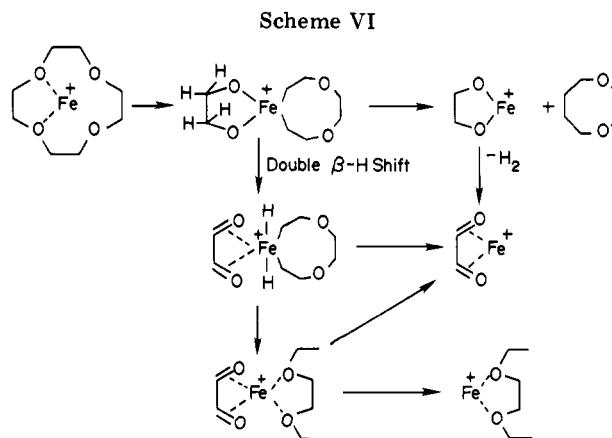
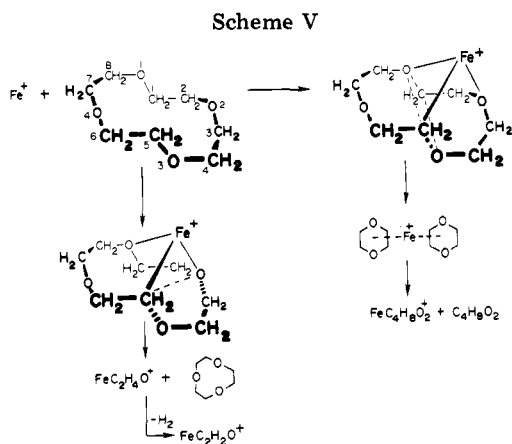
(17) All thermochemical values, unless otherwise noted, were obtained from: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* 1977, 6.

(18) Groth, P. *Acta Chem. Scand., Ser. A* 1978, A32, 279.

(19) Bystrom, K.; Mansson, M. *J. Chem. Soc., Perkin Trans. 2* 1982, 565.

Table VI. Ion-Molecule Reactions of Fe⁺ with 12-Crown-4

reaction	product distributn	see Scheme
$\text{Fe}^+ + \text{12-crown-4} \rightarrow \text{FeC}_2\text{H}_2\text{O}^+ + \text{C}_6\text{H}_{14}\text{O}_3 + \text{H}_2$	0.23	V
$\rightarrow \text{FeC}_2\text{H}_2\text{O}_2^+ + \text{C}_6\text{H}_{14}\text{O}_2 + \text{H}_2$	0.14	VI
$\rightarrow \text{FeC}_2\text{H}_4\text{O}_2^+ + \text{C}_6\text{H}_{12}\text{O}_2$	0.44	VI
$\rightarrow \text{FeC}_4\text{H}_4\text{O}^+ + \text{C}_4\text{H}_{10}\text{O}_3 + \text{H}_2$	0.02	VII
$\rightarrow \text{FeC}_4\text{H}_6\text{O}^+ + \text{C}_4\text{H}_{10}\text{O}_3$	0.01	VII
$\rightarrow \text{FeC}_4\text{H}_8\text{O}_2^+ + \text{C}_4\text{H}_8\text{O}_2$	0.13	V
$\rightarrow \text{FeC}_4\text{H}_8\text{O}_3^+ + \text{C}_4\text{H}_8\text{O}$	0.01	VII
$\rightarrow \text{FeC}_6\text{H}_{14}\text{O}_2^+ + \text{C}_2\text{H}_2\text{O}_2$	0.02	VI



ucts of Fe⁺ with 12-crown-4 are indicated in Table VI.

In some cases, Fe⁺ appears to break down the polyether into smaller cyclic ethers.¹⁵ One product, FeC₄H₈O₂⁺, appears to be the result of cleavage of 12-crown-4 into two 1,4-dioxane molecules. The process is favored since two molecules of 1,4-dioxane are approximately 20 kcal/mol more stable than one molecule of 12-crown-4.¹⁶

This rearrangement of 12-crown-4 is consistent with a distinct secondary structure for the polyether which is shown in Scheme V. This structure was derived from X-ray crystallographic studies.¹⁸ The molecule appears to have the same secondary structure in solution.¹⁹ 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.²⁰) Using the numbering scheme of Scheme V, 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. If Fe⁺ can complex with this ligand without extensive changes in the secondary structure, initial complexation with lone pairs on oxygen atoms 1 and 2 will direct the metal toward carbon 5. These three atoms are in close proximity in this model. Scheme V shows that such an initial interaction would lead to the FeC₄H₈O₂⁺ product. In Scheme V it is shown that Fe⁺ can bring oxygen 1 and carbon 5 in close proximity to form two rings. If this interaction brings carbon 5 and oxygen 2 in closer proximity, 9-crown-3 can be eliminated, leaving FeC₂H₄O⁺ which rapidly loses H₂ to form FeC₂H₂O⁺, 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 CH₂ unit (which

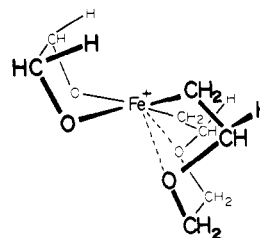


Figure 1.

is across the ring) in close proximity for initial interaction with the metal. 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 V. Many other products are more complicated than simple fragments of 12-crown-4 bound to the metal, but the products usually correspond to some fragment of the cyclic ether ± 2 u, indicative of two H shifts.²⁴ Many of the products can be explained by a double insertion mechanism, in which Fe⁺ inserts into two C-O bonds, followed by double β -H atom shifts. Scheme VI shows how this can occur to form FeC₂H₄O₂⁺, FeC₂H₂O₂⁺ (similar to a metal-butadiene complex), and FeC₆H₁₄O₂⁺. This mechanism has been discussed in a recent communication.⁸ Note that it also follows initial interaction with oxygen atoms 1 and 2. Following the double insertion, we again see a situation where both the "left" and "right" groups contain β -H atoms which could shift. Apparently only those on the "left" do. Molecular models suggest that further interaction of the

(20) Intramolecular hydrogen bonding in 12-crown-4 is suggested by Dale, J. *Isr. J. Chem.* 1980, 20, 3. Electron diffraction studies of similar polyethers do suggest one predominant configuration in the gas phase: Astrup, E. E. *Acta Chem. Scand. Ser. A* 1980, A34, 85.

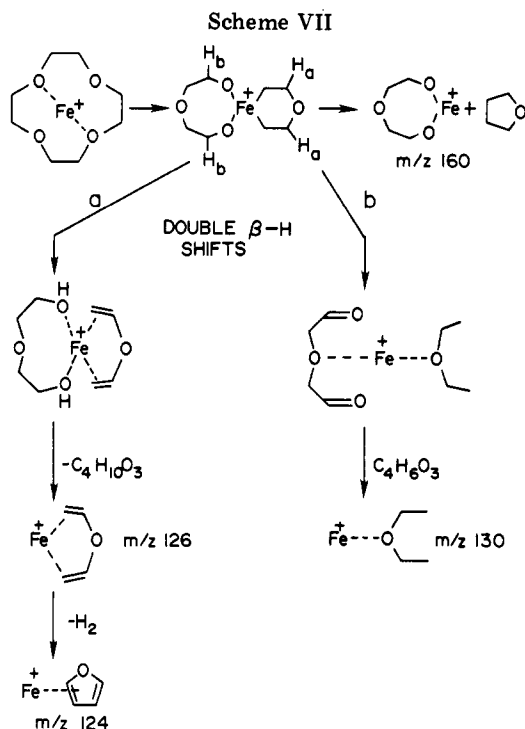
(21) See, for example: Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* 1979, 101, 4998.

(22) Allison, J. Ph.D. Thesis, University of Delaware, 1977.

(23) Tsaropoulos, A.; Allison, J., unpublished results.

(24) An alternate explanation would be, of course, two consecutive metal insertion, β -H shift sequences. H shifts may be sequential. While the authors prefer the simultaneous "double insertion", sequential insertions would avoid intermediates with unusually high (formal) oxidation states for the metal.

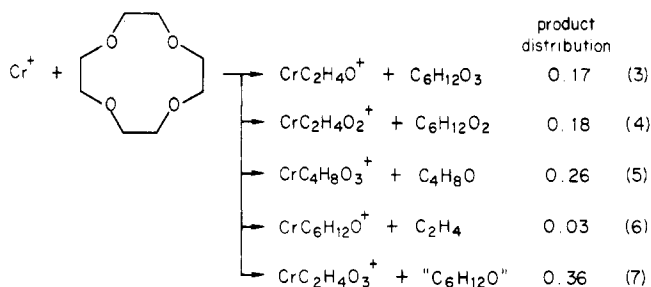
(25) One must, of course, be careful in drawing thermodynamic conclusions from such experiments. Electron impact on Cr(CO)₆ forms Cr⁺ in both the ground state and in a long-lived excited state (Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* 1980, 102, 7129. Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Ibid.* 1981, 103, 963.) This could affect the products observed in the Cr⁺ reactions.



oxygen on the "right" group with the metal 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 Figure 1, control the availability of β -H atoms for rearrangement.

Scheme VII predicts the remainder of the products through another double insertion, double β -H shift scheme. 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/z 130. An ion m/z 130 was observed but is not included in Table VI because of the unambiguous mass assignment (see Table V).

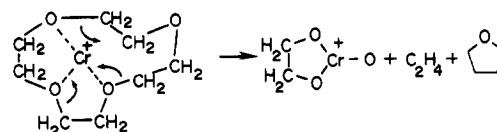
The chemistry of Cr^+ with 12-crown-4 differs from that of Fe^+ , apparently due to the fact that, relative to Fe^+ , Cr^+ interacts more strongly with oxygen and less strongly with carbon (eq 3-7).



The first product $\text{CrC}_2\text{H}_4\text{O}^+$ could be explained by using a mechanism similar to that in Scheme V. Note that, products in (4)-(6) (above) have ligands with a higher O:C ratio than those formed in Table VI with Fe^+ . Consider the product $\text{CrC}_2\text{H}_4\text{O}_2^+$. This could be considered either as Cr^+ complexed to $\text{OC}_2\text{H}_4\text{O}$ or as a metallocyclic five-membered ring. The latter will be assumed because of the strong $\text{Cr}^+\text{-O}$ 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 in (4)-(6) are shown in Scheme VIII. Note that all pairwise combinations of oxygens are sampled.

The products in (7) have a very high O:C ratio in the ionic product and may be the result of the small metal ion

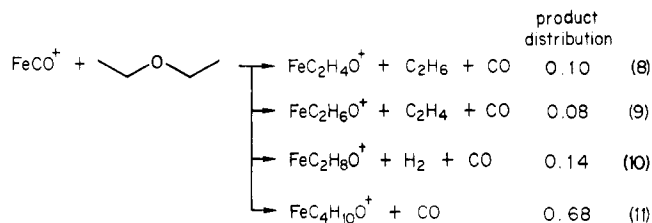
"puckering" up the molecule in an attempt to interact with three oxygens of the crown ether.



Loss of ethylene and THF as neutrals is shown here to be mechanistically accessible products. 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.

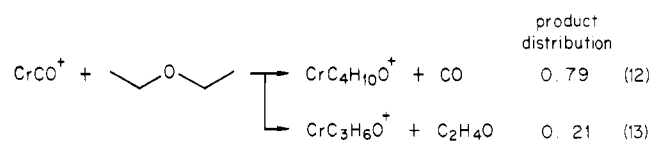
B. The Chemistry of CrCO^+ and FeCO^+ with Ethers and Polyethers. When one CO is added to the metal center, the reactivity with molecules containing more than one functional group can be dramatic.⁶ There are many instances where the CO acts not only as an "observer" ligand but becomes active in the reaction. That is, MCO^+ reacts through pathways in which metal ion insertion occurs and via insertion of the entire MCO unit into a C-O bond.

1. Diethyl Ether. With FeCO^+ and diethyl ether, the reactions are straightforward (eq 8-11).

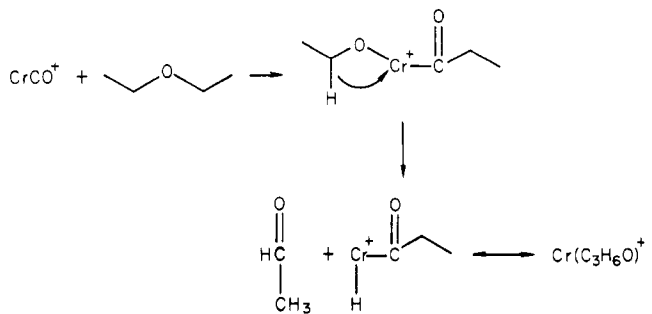


The processes in (8)-(10) were observed for Fe^+ alone and are presumed to occur by the same mechanism; however here we have concurrent cleavage of the $\text{M}^+\text{-CO}$ bond. Reaction 10 is a commonly observed ligand substitution.²¹

CrCO^+ reacts with diethyl ether to form two products (eq 12 and 13). Reaction 12 is a simple displacement of CO by the ether. Reaction 13 is unusual. $\text{CrC}_3\text{H}_6\text{O}^+$ is not a product observed in the reaction of Cr^+ with diethyl ether. If the metal inserted into a C-C bond, there would be no β -H atom available to shift and eliminate CH_4 .



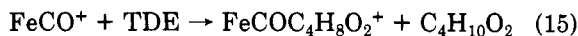
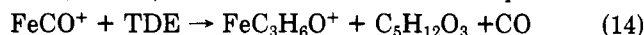
Thus, we conclude that the CO of CrCO^+ is actively involved in the process and inserts in toto into the O-C ether bond. On the basis of past observations, the neutral product of (13) could be $\text{C}_2\text{H}_4\text{O}$ or (CO and CH_4).



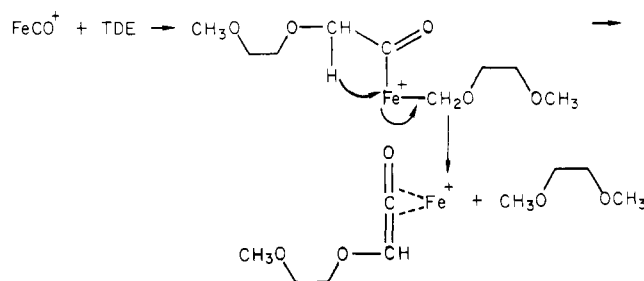
This mechanism leads to acetaldehyde as the neutral lost in (13).

2. Triethylene Glycol Dimethyl Ether (TDE). The reactions of MCO^+ with TDE are dramatically different than for M^+ alone.

$\text{Fe}(\text{CO})^+$ forms three products with TDE. One product, m/z 116, is listed in Table III as an ambiguous ion, $\text{FeCH}_3\text{OC}_2\text{H}_5^+$ or $\text{FeCOCH}_3\text{OH}^+$ both being possible structures (the methanol complex is preferred, since CrCH_3OH^+ is formed from the reactions of CrCO^+ with TDE). Also, FeCO^+ reacts as shown in eq 14 and 15.



$\text{FeC}_3\text{H}_6\text{O}^+$ (eq 14) was also formed by Fe^+ alone (Scheme III). In reaction 15, since (a) $\text{C}_4\text{H}_8\text{O}_2$ is not "extracted" from TDE by Fe^+ alone and (b) CO is retained, we interpret this as another MCO^+ insertion process, here 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- η^2 -ketene complex, which is frequently observed in such studies.⁹

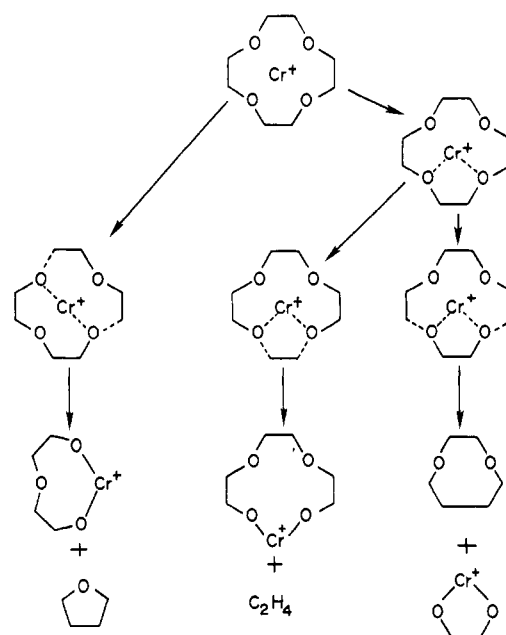
Recall that Cr^+ forms three products with TDE. CrCO^+ reacts to form nine products (eq 16–24).

The products in (16)–(18) were also formed by Cr^+ alone and thus have been discussed in Scheme IV. 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 $\text{CrCOCH}_3\text{OH}^+$ are products. Thus, we interpret this via a M^+ insertion process, in which the CO acts as a spectator ligand (Scheme IX). Once the metal center has induced the elimination of methanol from TDE, the $\text{Cr}^+(\text{CH}_3\text{OH})(\text{CO})$ can use the remaining available energy to break a Cr^+-CO bond.

The products in (22)–(24) can also be explained by CrCO^+ insertion into the central skeletal bond of TDE.

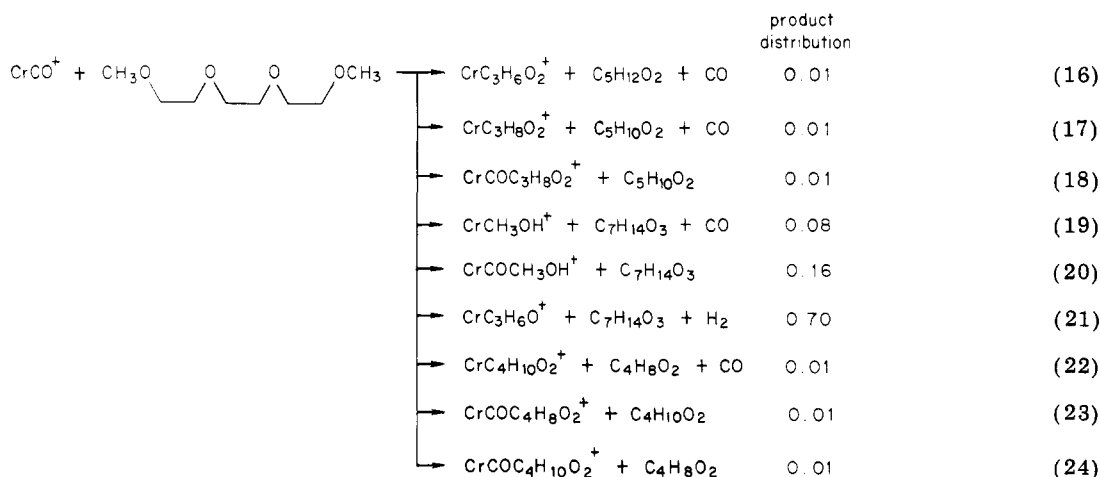
3. 12-Crown-4. CrCO^+ reacts with 12-crown-4 to form three products (see Table IV), all of which are also formed by Cr^+ alone. Thus, CO is a spectator in these reactions.

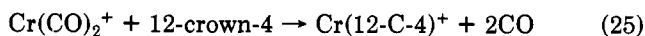
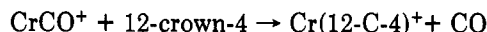
Scheme VIII



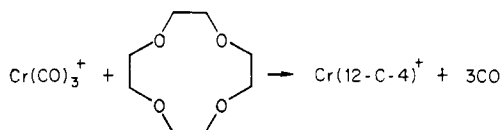
FeCO^+ forms seven products with 12-crown-4; six of them were also formed by Fe^+ alone (see Table V). Thus, MCO^+ insertion does not appear to predominate in the reactions with the cyclic polyether. The new product for FeCO^+ with 12-crown-4 is m/z 204, $\text{FeC}_6\text{H}_{12}\text{O}_4^+$, corresponding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

C. The Chemistry of the Higher $\text{M}(\text{CO})_x^+$ Ions with Ethers and Polyethers. In Table I it is apparent that, as the number of CO 's present on the metal increases, ligand substitution becomes the predominant process. Diethyl ether can displace up to three CO 's in the case of iron and up to two CO 's in the case of chromium. Always present in both mixtures is the metal-ether complex, $\text{M}(\text{C}_4\text{H}_{10}\text{O})^+$, formed by CO displacement. This is typical of other systems studied²¹—in fact most compounds which have been studied except alkyl fluorides^{22,23} have been observed to displace CO from charged transition-metal centers. In these studies involving TDE, 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 two precursors (eq 25).



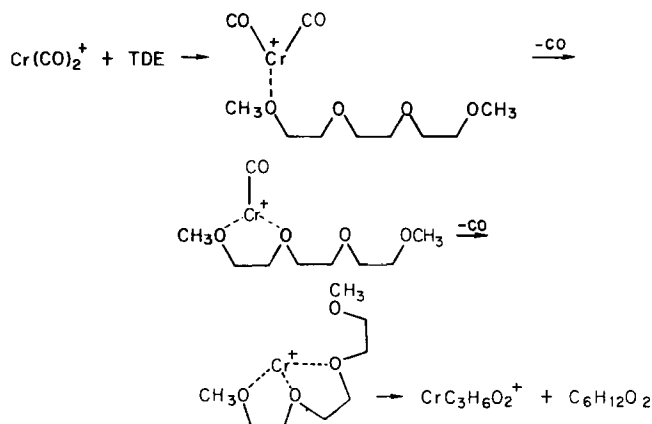


Since $\text{Cr}(\text{CO})_3^+$ is not a precursor to $\text{Cr}(12\text{-C-4})^+$, one may interpret this as an indication of the Cr^+ -crown bond strength $D(\text{Cr}^+-\text{CO}) + D(\text{CrCO}^+-\text{CO}) < D(\text{Cr}^+-12\text{-C-4}) < D(\text{Cr}^+-\text{CO}) + D(\text{CrCO}^+-\text{CO}) + D(\text{Cr}(\text{CO})_2^+-\text{CO})$; 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



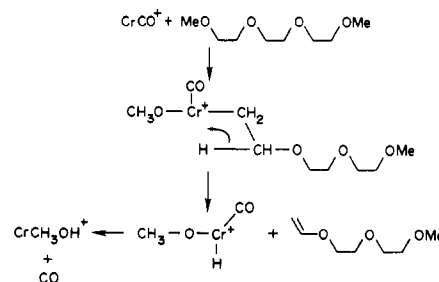
does not occur because the carbonyl ligands prevent this large ligand from getting close enough to the metal for significant orbital overlap. This is very graphically seen as we progress from diethylether to TDE to 12-crown-4. The reactions due to $\text{M}(\text{CO})_n^+$ decrease as n increases. The effect is even more graphic for 12-crown-4. Thus, reactions of M^+ alone are presumably due to the metal *in* the crown cavity. As CO's are added to the metal, reactions occur with the metal moved out of the cavity to the point where CO's prohibit metal-ligand interaction with this bulky ligand. This unusual lack of reactivity for the highly complexed metal centers with polyethers is indicated in Table VII.

A number of observations should be made in Table VII. In the case of diethyl ether, ions such as $\text{M}(\text{CO})_3^+$ and $\text{M}(\text{CO})_5^+$ are reactive, but only by ligand substitution. The reactivity (i.e., the *number* of products) increases as the neutral changes from an ether to a polyether. It is more striking to realize that *all* of the products for TDE are reactive rearrangements of 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, e.g.



In the case of 12-crown-4, however, it is much more difficult for the ether oxygens to bond stepwise to the metal. Thus, when the metal can get close enough to interact, a rich chemistry is observed. When three 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, are observed. Thus,

Scheme IX

Table VII. Number of Reaction Products Observed for Metal Centers^a in Various States of Coordination

reactant ion	Diethyl ether		TDE		12-crown-4	
	Cr ⁺	Fe ⁺	Cr ⁺	Fe ⁺	Cr ⁺	Fe ⁺
M ⁺	1	3	3	1	5	9
MCO ⁺	2	3	9	3	3	7
M(CO) ₂ ⁺	2	3	12	7	3	2
M(CO) ₃ ⁺	1	2	2	4	0	0
M(CO) ₄ ⁺	0	3	0	4	0	0
M(CO) ₅ ⁺	1	2	0	1	0	0
M(CO) ₆ ⁺	0		0		0	

^a M equals Cr⁺ or Fe⁺ as indicated.

it is difficult to interpret the data here in terms of estimating M^+ -polyether bond strengths. The Cr^+ -12-crown-4 bond strength, based on reaction 25, must be >66 kcal/mol.¹⁷

Summary and Conclusions

A number of conclusions can be drawn from this study: (a) The differences in the gas-phase chemistry of Cr^+ and Fe^+ with polyethers appear to be due to a large extent to the energies with which they interact with the skeletal units CH_2 and O.

(b) The chemistry of Fe^+ and Cr^+ with TDE resembles that for diethyl ether, in that similar mechanisms are operable for both.

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

(d) Many products of reactions involving 12-crown-4 can be explained by using a double metal insertion, double β -H shift process. In these reactions, CO ligands act predominantly as spectators.

(e) 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 greater than three CO's on a metal center may prohibit sufficiently close approach for interaction.

We are presently studying a number of other metal centers with 12-crown-4, 9-crown-3, 15-crown-5, and smaller cyclic polyethers such as the dioxanes in an attempt to better understand the complex metal-ligand interactions and rich chemistry reported here.

Acknowledgment is made to the Dow Chemical Co. foundation and the National Science Foundation (Grant CHE-8023704) for support of this work.

Registry No. $\text{C}_4\text{H}_{10}\text{O}$, 60-29-7; $\text{C}_8\text{H}_{18}\text{O}_4$, 112-49-2; $\text{C}_8\text{H}_{16}\text{O}_4$, 294-93-9; Fe^+ , 14067-02-8; Cr^+ , 14067-03-9.