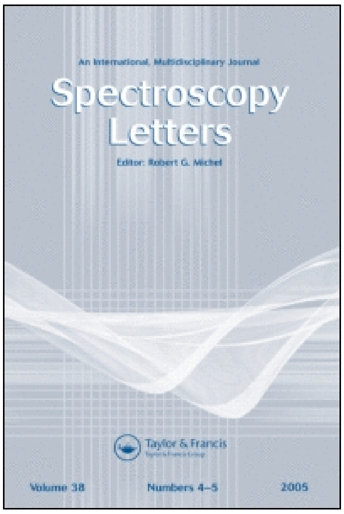

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A "Mechanistic" Macrocyclic Effect in the Gas Phase Chemistry of Metal Ions with Polyethers

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A "MECHANISTIC" MACROCYCLIC EFFECT IN THE GAS PHASE CHEMISTRY OF METAL IONS WITH POLYETHERS

Key Words: Ion Cyclotron Resonance Spectrometry; Metal Ions; Crown Ethers; 12-Crown-4.

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ABSTRACT

The stability of metal ion - polyether complexes for cyclic polyethers is greater than their linear analogs. This effect has been referred to as the macrocyclic effect. Here, we report a "mechanistic" macrocyclic effect observed in low pressure gas phase ion-molecule reactions involving transition metal ions and both linear and crown ethers. The crown ethers are much more reactive with Cr^+ and Fe^+ than their linear analog. Presumably, the cyclic ligand forces more parts of the molecule to interact with the metal ion, while only one part of the linear polyethers reacts with these metal centers.

INTRODUCTION

In 1969, Cabbiness and Margerum[1] first used the term *macrocyclic effect* in discussing the enhanced stability of metal

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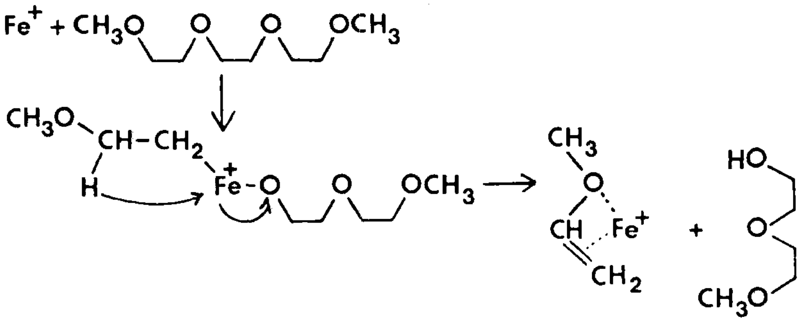
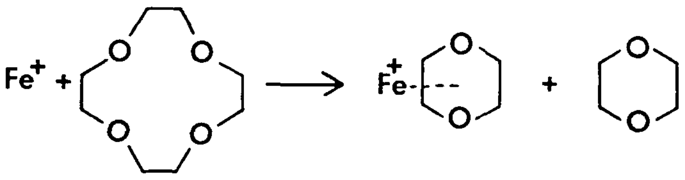
ion-macrocyclic ligand complexes over those involving the analogous linear ligand. Here, we report significant differences in the chemistries of gaseous metal ions with 12-crown-4 (12C4) and the linear analog, triethyleneglycoldimethylether (TDE). These bimolecular ion-molecule reactions were studied using Ion Cyclotron Resonance Spectrometry.[2]

Fe^+ (formed by electron impact on $Fe(CO)_5$) reacts with the linear polyether, TDE, to form only one product, $Fe(C_3H_6O)^+$. This can be easily explained by comparison to studies of Fe^+ with simple aliphatic ethers,[3] and using accepted mechanisms.[4] Apparently the metal ion inserts into a C-O bond, and a β-H shift follows to produce the observed product, (just as Fe^+ reacts with simple ethers such as diethylether).

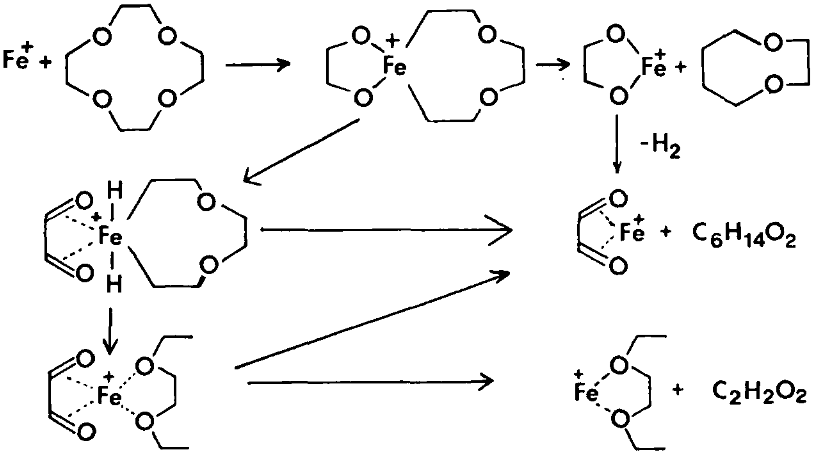


Fe^+ reacts with 12-crown-4, the cyclic analog, much differently, forming nine different products. While a complete discussion of all products will not be given here, reactions typical of those observed can be given. One type of reaction involves breakdown of the crown into smaller cyclic ethers, with cavity sizes more compatible with the small metal ion (d $\sim$ 1.0 Å).



Three additional products, $FeC_2H_4O_2^+$, $FeC_2H_2O_2^+$ and $FeC_6H_{14}O_2^+$ can be explained via one mechanistic pathway, which uses mechanistic steps similar to those for TDE (above), but indicative of a more complex metal-ligand interaction. With 12-crown-4, a number of products can be explained using a double-insertion step followed by a double-β-H atom shift. This is shown in Scheme 1.

The enhanced reactivity of the cyclic polyether over the linear case apparently is due to the fact that the cyclic ligand forces a greater number of the oxygen atoms into close (reactive) proximity with the metal ion during the brief ion-molecule col-

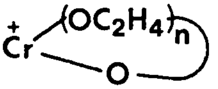


Scheme 1.

lision. That is, we are reporting a new, mechanistic aspect of the macrocyclic effect in these gas phase ion-molecule reactions. Such processes are not observed in solution, since the ion-ligand interaction energy is quickly dispersed to solvent molecules.

We assume that, in the case of 12-crown-4, the Fe^+ actually induces these 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 one product, 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 reactions.

Also of note is the fact that Cr^+, a first row transition metal ion similar in size to Fe^+, forms very different products with 12-crown-4 and TDE than does Fe^+, i.e. Cr^+ reacts with 12-crown-4 to form products of the type.



n = 1,2,3

Apparently the strength of the Cr^+-O bond[5] dominates the reactivity of this metal ion with 12-crown-4.

Currently we are studying the chemistry of a number of gaseous metal ions with linear and cyclic ethers and polyethers in the absence of solvent. We are attempting to determine why the reaction products of MCO^+ differ from those of M^+, and to what extent the metal ions can interact with such (possibly) multidentate ligands.

ACKNOWLEDGEMENTS

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