a strained double bond[6] in the reactant, which results in a stereospecific reaction, may be an example of dynamic control in the excited state, but only detailed dynamics computations could confirm this.

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The Gas-Phase Macrocyclic Effect: Reaction Rates for Crown Ethers and the Corresponding Glymes with Alkali Metal Cations

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The macrocyclic effect,[1] well-known in solution,[2] is manifested by higher binding constants and greater guest selectivity for cyclic as opposed to acyclic ligands. This effect is dramatically evident when the chemistry of the macrocyclic crown ethers is compared to that of their acyclic polyether analogues, the glymes.[2] For example, 18-crown-6 has binding constants in methanol 3–4 orders of magnitude higher for Na^+, K^+, and Ba^{2+} than does its acyclic analogue, pentaglyme.[3,4] Two factors are believed to be responsible.[5] First, the configurational entropy is more favorable for the cyclic ligands, since their donor groups are preorganized to interact favorably with a guest species, while acyclic ligands must undergo more extensive rearrangement to adopt a favorable conformation for guest binding. Second, because desolvation of both the ligand and the metal cation precedes complex formation, ΔH for the complexation process is more favorable for cyclic ligands, since they are less well-solvated than their acyclic counterparts. For nitrogen macrocycles in solution, the solvation effects dominate,[5] but it has proven difficult to generalize this observation for polyethers.[2,4] To eliminate the role of the solvent in such interactions and thereby observe the *intrinsic* reactivity of macrocyclic ligands, we have undertaken a study of the reactions of crown ethers and glymes with alkali metal cations in the gas phase. We report herein the observation of a strong gas-phase macrocyclic effect, which is evident in the kinetics of formation of metal cation-bound ligand dimer species.

Our studies build upon a number of earlier investigations of crown ether–cation interactions in the gas phase, which employed fast atom bombardment[6] (FAB) and plasma desorption[7] mass spectrometry, as well as studies of the mass spectrometry of crown ethers[8] and their gas-phase reactions[9,10] with Fe^+ and Co^+. The transition metal experiments are particularly interesting in that they exhibit a "mechanistic" macrocyclic effect: 12-crown-4 reacting with Fe^+ gave nine products, but triglyme gave only one.[9,10] Likewise, Cr^+ gave five products with 12-crown-4 but only three with triglyme.[10] These results clearly warrant further investigation.

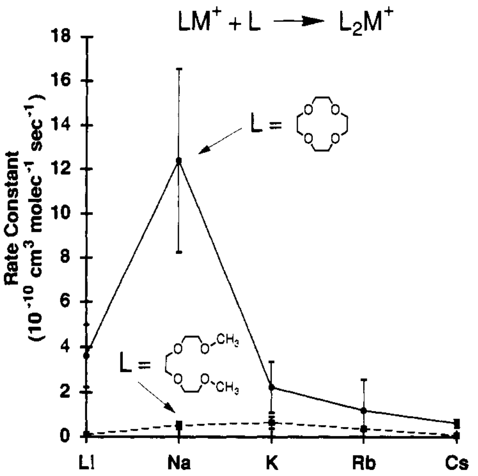

Figure 1. Mean rate constants for formation of alkali metal cation-bound dimers of 12-crown-4 and triglyme. Error bars are ± 1 standard deviation.

Our experiments were performed using a Fourier transform ion cyclotron resonance mass spectrometer (Extrel FTMS-1000). Alkali metal cations were introduced into the trapping cell via laser desorption using an excimer pumped dye laser (Lambda Physik LPX 205i/FL 3002). A variable leak valve was used to admit neutral ligands into the vacuum chamber. The compounds employed were used as purchased, except that each was subjected to successive freeze–pump–thaw cycles prior to introduction into the leak valve. Pressures were measured with a Bayard-Alpert ionization gauge, which was calibrated by measuring rates for the self-chemical ionization of acetone and comparing the results to literature values.[11] Ligand pressures were typically in the range 5×10^{-8}–5×10^{-7} Torr. Rate constants were measured by monitoring reactant and product ion intensities as a function of time and applying pseudo-first-order kinetic analysis.

The largest likely source of error in the *absolute* rate measurements is in the pressure determinations. However, the *relative* rate constants determined using these methods are conservatively estimated to be correct within better than about ±33% based on the reproducibility of repetitive measurements. The pressure variable is essentially eliminated in the relative rate determinations, because up to four different alkali metal ions were simultaneously introduced into the trapping cell (by mixing their salts on the sample probe) and studied together under identical neutral pressures.

Subsequent to the laser shot, 1:1 ligand–alkali metal cation complexes were observed to form rapidly in the trapping cell. These complexes are probably radiatively stabilized.[12] Since the metal cations and the neutral ligands were introduced into the cell separately, this provides conclusive evidence that complex formation can occur as a gas-phase process, as had been suggested by earlier FAB experiments.[6,7] The observed complexation rates are within an order of magnitude of the ion–molecule collision

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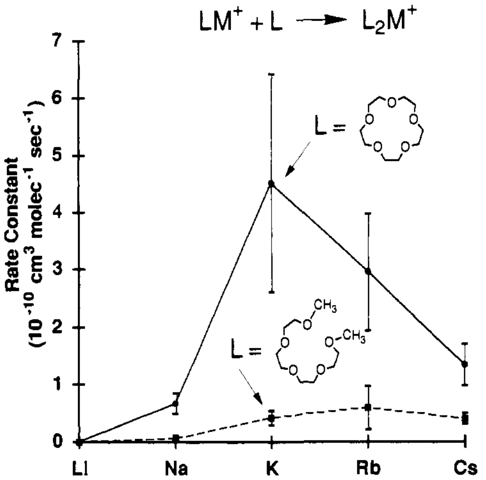

Figure 2. Mean rate constants for formation of alkali metal cation-bound dimers of 15-crown-5 and tetraglyme. Error bars are ± 1 standard deviation. The points for Li^+ are upper limits; dimer formation was not observed on the time scale of our experiment.

rate calculated using Langevin theory.[13] It is possible that complex formation occurs on every collision, and that differences between the observed complexation rates and the calculated collision rates are largely due to inaccuracies in our pressure measurements. If the rates do prove to be collision-limited, measurement of the complex formation rates will be a useful means of accurately determining the neutral ligand pressure in the trapping cell, which will enable more accurate absolute rate measurements for other reactions such as the formation of cation-bound dimers described below.

As we have previously noted,[14] the initially formed metal–ligand complexes undergo reaction with a second ligand to form metal-bound dimer species. For reaction times less than 500 ms, some curvature is evident in the plots of log (reactant intensity) versus time, suggesting that the reactant monomer complexes are incompletely cooled at short reaction times. Rate constants determined by fitting the later, linear portion of the plots are shown in Figures 1 and 2 for the four- and five-oxygen ligands, respectively. It is immediately apparent that rates for the macrocyclic ligands are approximately an order of magnitude faster than those for the glymes. In addition, the macrocycles show much more selective kinetics than the corresponding acyclic ligands, with rates peaking strongly for the first cation significantly larger than the ligand cavity. Thus, the maximum rate for formation of the alkali cation-bound dimer of 12-crown-4 occurs for Na^+, while for the 15-crown-5 ligand the rate is fastest for K^+. Rates for the glymes, which do not have a well-defined binding cavity, are much less cation-dependent and peak for the next larger alkali metal cation than do those for the crowns. This is consistent with the acyclic glymes being more flexible than the crowns in their ability to adopt configurations favorable for binding the larger metals. We are currently investigating cation–ligand binding affinities in the gas phase as a function of size and ligand cyclization, and it will be interesting to see whether or not there is any correlation between the reaction kinetics and energetics in these systems.

These results can be understood in terms of the relative ease with which the cyclic and acyclic ligands can accommodate cation guests. For example, molecular mechanics calculations[15] indicate that the intrinsic interaction energies of 18-crown-6 and pentaglyme with K^+ are similar. However, to convert the "all-trans" minimum energy conformation[16] of pentaglyme to the approximately D_{3d} conformation which provides optimum bonding to the cation, approximately 15 kcal mol^{-1} more energy is required than is needed for 18-crown-6 to adopt an optimal conformation.

Experimental proton affinity measurements also suggest that entropic effects are important. In the gas-phase protonation of crowns and acyclic polyethers, ΔS is much more favorable for macrocycles than for the corresponding glymes (12-crown-4, −8.3 cal K^{-1} mol^{-1}, vs triglyme, −18.3 cal K^{-1} mol^{-1}; 15-crown-5, −11.1 cal K^{-1} mol^{-1}, vs tetraglyme, −20.7 cal K^{-1} mol^{-1}).[17] Our data so far do not allow us to distinguish whether energetic or entropic effects dominate in explaining the differences between the cyclic and acyclic ligands.

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High Enantioselectivity for Intermolecular Cyclopropenation of Alkynes by Diazo Esters Catalyzed by Chiral Dirhodium(II) Carboxamides

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Functionalized cyclopropenes are viable synthetic intermediates whose applications,[2] which extend to a wide variety of carbocyclic and heterocyclic systems, are largely ignored because of the relative inaccessibility of these strained compounds. However, recent advances in the synthesis of cyclopropenes, particularly from rhodium(II) carboxylate catalyzed reactions of diazo esters in the presence of alkynes,[3-5] have made available an array of stable 3-cyclopropenecarboxylate esters. Previously, copper catalysts provided low to moderate yields of cyclopropenes in reactions of diazo esters with disubstituted acetylenes,[3a,6] but the higher temperatures required for these carbenoid reactions often led to thermal or catalytic ring opening and products derived from

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