LASER FLASH PHOTOLYSIS, EPR AND RAMAN STUDIES
OF LIQUIDS AT ELEVATED PRESSURES

Progress Report
for Period April 1, 1993 - November 19, 1993

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November 19, 1993

Prepared for

THE U.S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG03-93ER14340

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Progress Report Abstract

A laser flash photolysis kinetic study of a $W(CO)_6$ intermediate reacting with several different substituted 2,2'-bipyridine ligands at pressures up to 150 MPa in liquid toluene has confirmed the considerable influence of steric hindrance on the mechanism of a thermal ring closure reaction. A similar laser flash photolysis kinetic study has been carried out with $Mo(CO)_6$ and several bidentate ligands resembling 2,2'-bipyridine dissolved in supercritical carbon dioxide. A much larger negative activation volume is found in supercritical carbon dioxide than was observed previously with this solute system dissolved in liquid toluene. The rate of replacement of one polydentate ligand by another stronger chelating agent in the first coordination sphere of aqueous gadolinium(III) ion was measured over a range of pressures and other variables using a stopped-flow spectrophotometer. Two consecutive first order reaction steps are observed that show acid-catalysis.

N O T I C E

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In the seven and one half months that have elapsed since April 1, 1993 (when the present three year grant period started), we have completed the experimental work on three scientific papers.

The first of these papers is entitled "Can Steric Hindrance Cause a Gradual Change in the Ring-Closure Mechanism of Complexes of the Type $W(CO)_5N-N$, Where N-N Represents a Series of Substituted Bipyridine Ligands?" The abstract of this paper reads as follows: The kinetics of the thermal ring-closure reactions of $W(CO)_5L$, produced during the photolysis of $W(CO)_6/L$, where $L = 2,2'$ -bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 4,4'-diphenyl-2,2'-bipyridine and 4,4'-di-*tert*-butyl-2,2'-bipyridine, were studied as a function of pressure. The values of the activation parameter $\Delta V^\ddagger$ are small and negative for these ligands, supporting an associative interchange mechanism (I_a) for CO extrusion. The $\Delta V^\ddagger$ values exhibit a specific trend toward more positive values on increasing the steric hindrance on the ligand. This trend is interpreted as evidence for a gradual change in mechanism from a more associative to a more dissociative ring-closure process.

The flash photolysis experiments carried out in the above described study involved the use of a Q-switched, frequency tripled Nd:YAG laser and a home-made, three-window, high pressure autoclave with a quartz pill-box sample cell insert. This paper was submitted for publication in August, 1993 and is scheduled to appear in print in January, 1994.

Similar laser flash photolysis experiments were also carried out on molybdenum hexacarbonyl sample systems dissolved in supercritical CO_2 . A thermal ring closure reaction of the species $Mo(CO)_5L$ where L is pyridine, 2,2'-bipyridine or 1,10-phenanthroline is found to proceed at rates comparable to those measured previously in liquid benzene or toluene. A much larger

negative $\Delta V^\ddagger$ is found for the 2,2'-bipyridine thermal ring closure reaction in supercritical CO_2 than in liquid toluene. Coordination of CO_2 with the molybdenum complex is sufficiently strong to produce a reaction path for the 1,10-phenanthroline ring closure reaction in supercritical CO_2 that is not seen in liquid toluene.

These supercritical CO_2 experiments were carried out with a syringe pump loaned to us by Professor Milton L. Lee (B.Y.U.). The key to making these experiments work was the development in our laboratory of a sample cell with a long capillary inlet for insertion in the high pressure autoclave. The long capillary prevents the $\text{Mo}(\text{CO})_6$ and bidentate ligands from escaping from the sample cell when it is depressurized. A first draft of this manuscript has been circulated to the coauthors, and it should be ready for submission for publication in another month.

The thermodynamics and kinetics of reactions between trivalent lanthanide cations, Ln^{3+} , and polydentate anionic ligands are important in the separation of the lanthanide elements, and in their uses as contrast-enhancing agents in magnetic resonance imaging and as radiopharmaceuticals. It is well known that the substitution reactivity of Ln^{3+} complexes varies strongly within the lanthanide series and reaches a maximum between Sm^{3+} and Gd^{3+} . This is attributed to a changeover in coordination number from 9 for the earlier, lighter members to 8 for the later, heavier members of the series when water is the solvent. Water exchange on $\text{Ln}(\text{H}_2\text{O})_9^{3+}$ takes place via an associative interchange (I_a) mechanism, whereas water exchange on $\text{Ln}(\text{H}_2\text{O})_8^{3+}$ follows a dissociative interchange (I_d) mechanism. In a fruitful two month sabbatical leave visit to our laboratory Professor Rudi van Eldik completed a collaborative stopped-flow spectrophotometric kinetic study of the replacement

of arsenazo III by edta or dtpa in the first coordination sphere of aqueous gadolinium(III) ion. Reaction rates were studied as a function of chelating ligand concentration, pH, temperature and pressure. Under all experimental conditions two consecutive reaction steps were observed, for which the observed first-order rate constants are independent of ligand concentration and show significant acid-catalysis. The observed kinetic behavior and the activation parameters determined under limiting conditions, i.e. low and high $[H^+]$, can be accounted for in terms of the dechelation of the arsenazo III ligand being the rate determining step. We have postulated the existence of 1:1 and 1:2 Gd(III): arsenazo III complexes to account for the fast and slow substitution reactions, respectively. The observed volumes of activation can mainly be ascribed to large solvational changes associated with the acid-catalyzed dechelation process.

This kinetic study of the chelation kinetics of aqueous gadolinium(III) was carried out on a homemade, high-pressure, stopped flow apparatus. The work was greatly facilitated by the purchase of the OLIS KINFIT software to interpret the experimental PMT voltage versus time curves.

Two review articles describing photoacoustic spectroscopic techniques have also been written during the past seven and a half months.

Personnel

Persons paid from DOE grant funds during the progress report period include (in alphabetical order): Shibai Cao (graduate student), Edward M. Eyring (principal investigator), Huaying Huai (postdoctoral associate), Qin Ji (graduate student), Marilyn Masiker (graduate student), and Rudi van Eldik (visiting professor).

Publications Acknowledging Support of this Grant Since April 1, 1990

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