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PULSED LASER KINETIC STUDIES OF LIQUIDS
UNDER HIGH PRESSURE

Progress Report
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Pulsed Laser Kinetic Studies of Liquids Under High Pressure

Progress Report Abstract

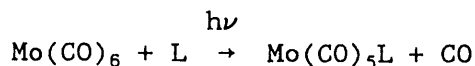
A laser flash photolysis kinetic study of 2,2'-bipyridine bidentate chelating ligands with one claw in the first coordination sphere of a molybdenum carbonyl complex has been completed at pressures up to 150 MPa. The reaction mechanism for thermal ring closure is found from activation volumes to change from associative interchange to dissociative interchange as substituents on the 2,2'-bipyridine ligands become bulkier. In a similar study of more rigid, substituted phenanthroline bidentate ligands it was found that substituent bulkiness had little effect on the thermal ring closure mechanism. Stability constants for lithium ion complexes with crown ethers in a room temperature molten salt, fluorescence quantum yields for cresyl violet and several other dyes in solution, and the oxidation of alcohols by OsO_4 have also been investigated.

N O T I C E

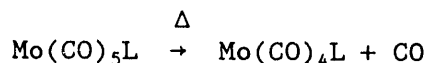
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Since late November of 1991, significant progress has been made on several research projects. [The superscripted footnote numbers refer to the list of publications acknowledging financial support by this grant and to a list of invited talks describing our DOE funded research both located on pages 6 and 7 of this report.]

Ultraviolet laser flash photolysis of Mo(CO)_6 in the presence of a ligand L generates $\text{Mo(CO)}_5\text{L}$ in toluene solution:



If L is a bidentate ligand, the primary photolysis product undergoes a comparatively slow (time constant τ of seconds) thermal ring closure reaction:



When the rate of the ring closure reaction is measured spectrophotometrically at several pressures between 1 atm and 1500 atm the reaction mechanism can be deduced from the resulting activation volumes.

A paper⁶ describing such a kinetic study using the ligands, 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy) and 4,4'-diphenyl-2,2'-bipyridine (dpbpy) required a Turbo Pascal-based computer program to interpret the kinetic traces of optical transmittance at $\lambda = 495$ nm versus time. This home made computer program was completed in December, 1991, and a manuscript was submitted for publication in late January, 1992. In essence, this paper⁶ reports activation volumes for ring closure ranging from -7.0 to +4.7 $\text{cm}^3 \text{mol}^{-1}$ from which we inferred that the reaction mechanism changes from associative interchange (I_a) to dissociative interchange (I_d) because of increasing steric hindrance as the ligand L becomes bulkier.

A similar high pressure kinetic study of ring closure in $\text{Mo(CO)}_5\text{L}$ in which the ligands are more rigid phenanthrolines (5-chloro-1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, and 4,7-diphenyl-1,10-phenanthroline) revealed that steric effects from bulky substituents on the more rigid phenanthroline ligand have considerably less effect on the thermal ring closure mechanism than we had observed with flexible bipyridine ligands. The ring closure of these rigid phenanthroline chelates goes by an interchange (I) mechanism in which bond formation and bond cleavage at the Mo

center occur to a similar degree in the transition state independent of the size of the substituent groups on the phenanthroline chelate. A paper⁷ describing this study was accepted for publication by the Journal of Organometallic Chemistry on May 20, 1992.

If substituents on phenanthroline ligands make little difference to the mechanism of thermal chelate ring closure, it then becomes interesting to know whether changing the size of the Mo metal center to a smaller Cr metal center or a larger W metal center will have a major impact on the mechanism of thermal ring closure. Experiments in a laser flash photolysis study of the kinetics of tungsten carbonyl complex, $W(CO)_5L$, ring closure are largely completed with several phenanthroline ligands, and a manuscript will soon be ready for publication.¹² The recent results of our laser flash photolysis studies of thermal ring closure reaction mechanisms were reported in an invited paper at a regional American Chemical Society symposium¹³ and at a national meeting.¹⁴

A high pressure stopped-flow spectrophotometer is under construction in our departmental machine shop. It will be used to extend our laser flash photolysis kinetic experiments to a shorter time scale (5 msec to 1 sec).

With borrowed instrumentation from the laboratory of Prof. Milton Lee (B.Y.U.) we have carried out some supercritical fluid CO_2 experiments that should lead to mechanistic studies of these same metal carbonyl ring closure reactions in supercritical fluid (SF) solvent systems. We have dissolved molybdenum hexacarbonyl and a bidentate ligand in supercritical CO_2 and have observed the solution change from colorless to light yellow when illuminated with ultraviolet pulses of light from the Nd:YAG laser. Quantitative kinetic measurements have been delayed by the full time use of our Nd:YAG laser in the metal carbonyl flash photolysis experiments noted above.

In other research areas not involving high pressure liquids we have also made substantial progress. A room temperature molten salt was the medium in which we gathered 7Li -NMR data for the complexation of Li^+ by four different simple crown ethers [12-crown-4, 15-crown-5, benzo-15-crown-5 and 18-crown-6]. The greatest complex ion strength was found for the $Li^+/15$ -crown-5 complex that corresponds to the best size fit of the crown ether ligand cavity (0.85 Å radius) to the lithium ion (0.74 Å radius). This work was presented at an international meeting¹⁵ and will also soon appear in print.⁸

No experiments were done with our photothermal laser beam deflection apparatus during the present reporting period. However, results obtained previously are being published^{4,5,9} and have been reported in invited papers at two recent scientific meetings.^{16,17} An interesting insight from these studies is that the workhorse for gathering relative fluorescence quantum yields (using cresyl violet in methanol as a standard) was a Perkin-Elmer MPF-66 fluorescence spectrophotometer that represents pre-laser technology. However, the complete story being reported in three papers^{4,5,9} could not have been told without the absolute fluorescence quantum yield dependence on concentration of cresyl violet in methanol⁴ obtained with a pulsed, tunable dye laser in a photothermal beam deflection experiment. All the beam deflection and classical fluorescence studies were done by Stefan Isak who defended his Ph.D. thesis on February 27, 1992. He is now employed by Sandoz Pharmaceuticals Corporation in East Hanover, New Jersey doing chromatographic separations.

An unpaid Master of Science degree student, Jihee Ku, completed a rate study of the oxidation of alcohols by OsO_4 in alkaline aqueous solutions¹¹ using DOE funded supplies and equipment. The rates of these reactions are quite slow, so the principal experimental tool was a Hewlett-Packard 8452A diode array UV-VIS spectrophotometer. Ms. Ku found evidence from Hammett plots and kinetic isotope effects for a hydride ion transfer reaction mechanism.

Personnel

Persons paid from this grant during the progress report period include (in alphabetical order): Shibai Cao, graduate student; Edward M. Eyring, principal investigator; Stefan J. Isak, graduate student; Qin Ji, graduate student; Gabor Konya, graduate student; K. Bal Reddy, postdoctoral research associate; Barbara Staker, draftsman; and Paul Thompson, postdoctoral research associate.

Publications Acknowledging Support of this Grant Since April 1, 1990

1. E.M. Eyring, S.J. Komorowski, N.F. Leite, and T. Masujima, "Photoacoustic Instrumentation," *in* Analytical Instrumentation Handbook, G. W. Ewing, Editor, Marcel Dekker, New York, 1990, Chapter 10, pp. 337-360.
2. D. P. Cobranchi, N. F. Leite, J. Isak, S. J. Komorowski, A. Gerhard and E. M. Eyring, "Pulsed Laser Photothermal Radiometry and Photothermal Beam Deflection Spectroscopy: Determination of Thermal Diffusivities of Liquids," *in* Photoacoustic and Photothermal Phenomena II (Springer Series in Optical Sciences Vol. 62), J. C. Murphy, J. W. MacLachlan Spicer, L. C. Aamodt, and B. S. H. Royce, Editors, Springer-Verlag, New York, 1990, pp. 328-330.
3. S. J. Isak, B. A. Garland, E. M. Eyring, J. P. Kirkland and R. A. Neiser, "Photoacoustic Signal Enhancement at Visible and X-ray Wavelengths", *Appl. Phys. B*, 52, 8-13 (1991).
4. S. J. Isak and E. M. Eyring, "Fluorescence Quantum Yield of Cresyl Violet in Methanol and Water as a Function of Concentration," *J. Phys. Chem.*, 96, 1738-1742 (1992).
5. S. J. Isak and E. M. Eyring, "Cresyl Violet Chemistry and Photophysics in Various Solvents and Micelles," *J. Photochem. & Photobiol. A:Chem.*, 64, 343-358 (1992).
6. K. B. Reddy, R. Hoffmann, G. Konya, R. van Eldik and E. M. Eyring, "Thermal Ring Closure in Mo(CO)₅L (L = bpy, dmbpy, dpbpy) Transients Generated by Pulsed Laser Flash Photolysis. Mechanistic Information from High Pressure Effects," *Organometallics*, 11, 2319-2322 (1992).
7. K. B. Reddy, R.B. Brady, E.M. Eyring and R. van Eldik, "Effect of Pressure on Intramolecular Ring-Closure Reactions of Molybdenum Carbonyl Complexes Induced by Flash Photolysis," *J. Organometallic Chem.*, in press.
8. E.M. Eyring, D.P. Cobranchi, B.A. Garland, A. Gerhard, A.M. Highley, Y.-H. Huang, G. Konya, S. Petrucci and R. van Eldik, "Lithium Ion-Crown Ether Complexes in a Molten Salt," *Pure & Appl. Chem.*, in press.
9. S. J. Isak and E. M. Eyring, "Low Fluorescence Quantum Yields of Several Potential Photothermal Sensitizing Direct Blue Dyes," in preparation.
10. T. Masujima and E.M. Eyring, "X-Ray Thermal NDE," *in* Progress in Photothermal and Photoacoustic Science and Technology, Vol. II, Nondestructive Evaluation (NDE), A. Mandelis, Ed., Elsevier Science Publishing Co., New York, in preparation.

11. J. Ku, S. Cao, K.B. Reddy and E.M. Eyring, "Kinetics of Oxidation of Alcohols by OsO_4 in an Aqueous Alkaline Medium: Evidence from Substituent and Kinetic Isotope Effects for a Hydride Ion Transfer Mechanism," in preparation.
12. S. Cao, K.B. Reddy, E.M. Eyring and R. van Eldik, "Mechanistic Study of Thermal Ring Closure in $\text{W}(\text{CO})_5\text{L}$ (L = bpy, phen and Substituted Analogues) Using a High Pressure, Laser Flash Photolysis Technique," in preparation.

Oral presentations of DOE funded research during this reporting period:

13. E.M. Eyring, K.B. Reddy, R. Hoffman, G. Konya and R. van Eldik, "Pulsed Laser Kinetic Studies of Liquids Under High Pressures," 47th Northwest Regional American Chemical Society Meeting, University of Montana, Missoula, MT, June 16-19, 1992.
14. K.B. Reddy, R. Hoffman, G. Konya, R. van Eldik, and E.M. Eyring, "Thermal Ring Closure in $\text{Mo}(\text{CO})_5\text{L}$ (L = bpy, dmbpy, dpbpy) Transients Generated by Pulsed Laser Flash Photolysis. Mechanistic Information from High Pressure Effects," 203rd ACS National Meeting, San Francisco, CA, April 5-10, 1992, Inorganic Paper #628.
15. E.M. Eyring, D.P. Cobranchi, B.A. Garland, A. Gerhard, A.M. Highley, Y.-H. Huang, G. Konya, S. Petrucci and R. van Eldik, "Lithium-Crown Ether Complexes in a Molten Salt," 17th International Symposium on Macrocyclic Chemistry, Provo, UT, August 9-14, 1992.
16. E.M. Eyring, "Spectroscopic Applications of Photothermal Beam Deflection," 1992 Gordon Research Conference on Photoacoustic and Photothermal Phenomena, Colby Sawyer College, New London, NH, June 8-12, 1992.
17. S.J. Isak and E.M. Eyring, "Fluorescence and Nonradiative Decay Quantum Yields of Cresyl Violet and Other Dyes Measured by Photoacoustic, Photothermal and Standard Fluorescence Techniques," 45th Annual Summer Symposium on Analytical Chemistry: Fluorescence and Photothermal Spectroscopies, Utah State University, Logan, UT, June 23-25, 1992.

END

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