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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 high pressure apparatus constructed for measuring the rates of reactions in liquids under pressures ranging from 1 atm to 2000 atm has been used to measure the complexation kinetics of molybdenum hexacarbonyl reacting with 2,2-bipyridine, 4,4'-dimethyl-2,2'-bipyridine and 4,4'-diphenyl-2,2'-bipyridine in toluene. Pentacarbonyl reaction intermediates are created by a 10 nsec flash of frequency tripled Nd:YAG laser light. Measured activation volumes for chelate ligand ring closure indicate a change in mechanism from associative interchange to dissociative interchange as steric hindrance increases. A similar high pressure kinetics study of molybdenum carbonyl complexation by several substituted phenanthrolines is now well advanced that indicates that with the more rigid phenanthroline ligands steric effects from bulky substituents have less effect on the ring closure mechanism than in the case of the bipyridine ligands. An experimental concentration dependence of the fluorescence quantum yield of cresyl violet has been harmonized with previously published contradictory reports. Fluorescence of cresyl violet in various solvents and in micellar systems has also been systematically explored.

N O T I C E

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In the previous twelve months significant progress has been made on three research projects. [The superscripted footnote numbers refer to the list of publications acknowledging financial support by this grant on page 5.]

Ultraviolet 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 2000 atm the reaction mechanism can be deduced from the resulting activation volumes. K. B. Reddy and R. Hoffmann completed such a kinetic study recently using the ligands, 2,2-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy) and 4,4'-diphenyl-2,2'-bipyridine (dbpby). The activation volumes for ring closure range from -7.0 to +4.7 $\text{cm}^3 \text{mol}^{-1}$. Thus it appears that the mechanism changes from associative interchange (I_a) to dissociative interchange (I_d) because of increasing steric hindrance as the ligand L becomes bulkier. A computer program to analyze the precision of the experimental data is being written. The resulting paper⁶ is otherwise ready to submit for publication.

A similar high pressure kinetic study by Dr. Reddy of ring closure in $\text{Mo(CO)}_5\text{L}$ in which the ligands are more rigid phenanthrolines is now well advanced. (The ligands are 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.) The activation volume data for the ring closure reaction indicate that steric effects from bulky substituents on these phenanthrolines play a less decisive role in determining the reaction mechanism than in the previous study of the more flexible bipyridines. A manuscript⁷ reporting these results will be ready for publication by the end of calendar year 1991.

Stefan Isak's study of a concentration dependence of the fluorescence quantum yield of cresyl violet was finally accepted for publication⁴ after we developed a plausible explanation for a contradictory conclusion published previously [D. Magde *et al.*, J. Phys. Chem., **83**, 696 (1979).] During 1991, Isak completed another study⁵ of the chemical and physical behavior of cresyl violet perchlorate in aqueous micellar and organic solutions. This study was prompted by interest in cresyl violet as a laser dye and the well known use of micellar dye solutions in tunable dye lasers. An interesting rationale was developed for Isak's observation that fluorescence is quenched by surfactants with increasing effectiveness in the order aqueous sodium dodecyl sulfate (SDS), aqueous cetyltrimethylammonium bromide (CTAB), and aqueous Triton X-100 (a nonionic surfactant).

Most recently Isak has explored⁸ the potential effectiveness of one triazo and seven diazo dyes as photothermal sensitizers for laser photodynamic therapy of cancer. Isak has found the eight dyes studied (including Trypan Blue and Evans Blue) are very resistant to photobleaching, have no detectable triplet state populations, and have fluorescence quantum yields Φ_f less than 10^{-3} . These properties make the dyes studied particularly suitable for photodynamic therapy of cancer by radiationless decay.

During the summer of 1991, Dr. Achim Gerhard and Aaron Highley, a Yale undergraduate, prepared a new set of crown ethers dissolved with LiClO_4 in a room temperature molten salt (55/45 mole % 1-methyl-3-ethylimidazolium chloride/ AlCl_3). These solutions were subjected to ^7Li NMR measurements in autumn, 1991 and a paper reporting stability constants as well as ΔH and ΔS values for complex ion formation is being written.⁹

Personnel

Persons paid from this grant during the progress report period include (in alphabetical order): Edward M. Eyring, principal investigator; Achim Gerhard, postdoctoral research associate; Aaron Highley, undergraduate chemistry major; Rüdiger Hoffman, graduate student; Stefan J. Isak, graduate student; and K. Bal Reddy, postdoctoral research associate.

Publications Acknowledging Support of this Grant Since April 1, 1990

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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.
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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.*, in press.
5. S. J. Isak and E. M. Eyring, "Cresyl Violet Chemistry and Photophysics in Various Solvents and Micelles," submitted to *J. Photochem. & Photobiol.*
6. K. B. Reddy, R. Hoffmann, 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," in preparation.
7. K. B. Reddy, R. van Eldik and E. M. Eyring, "Dependence of Volume of Activation on Size of Substituent Groups in a Thermal Ring Closure of $\text{Mo}(\text{CO})_5\text{L}$ (L ~ Phenanthrolines) Produced by Pulsed Laser Flash Photolysis," in preparation.
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9. A. Gerhard, Y.-H. Huang, B. A. Garland, D. P. Cobranchi, A. Highley, G. Konya and E. M. Eyring, "Stability Constants and ΔH° Values for Lithium Ion Complexation by Crown Ethers in a Room Temperature Molten Salt," in preparation.

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