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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 has been constructed for measuring rates of reactions in liquids under pressures ranging from 1 atm to 2000 atm. This apparatus is being used to test the effect of ligand bulk on the rate of a thermal ring closure reaction. Microphonic photoacoustic signals obtained by illuminating solid samples with synchrotron soft X-rays and with visible laser beams have been successfully correlated with a theory for photoacoustic signal enhancement by volatile liquids. The concentration dependence of the fluorescence and nonradiative quantum yields for cresyl violet dissolved in methanol has been determined. Stability constants for complexes of lithium ion with four different crown ethers dissolved in a low temperature molten salt have been measured.

Since the last technical report of progress for this contract was written in September, 1989, substantial progress has been made in four research areas:

A high pressure apparatus was constructed in Germany following the designs of Professor Rudi van Eldik. E. M. Eyring went to Germany in May, 1990, to participate in the assembly and testing of this equipment. The apparatus was then disassembled, brought to Utah and reassembled by a graduate student, Bernice Kickel. She and an undergraduate student, Ryan Brady, during the summer of 1990 reproduced a recently published experiment [K. B. Reddy and R. van Eldik, Inorg. Chim. Acta 169, 13 (1990)]. In this experiment the kinetics of a reaction between tungsten carbonyl and 2,2'-bipyridyl are followed spectrophotometrically at λ = 514 nm on a time scale of seconds after the reaction is initiated by a flash of near ultraviolet light from a xenon arc lamp. The reaction is

$$W(CO)_6 + bpy \xrightarrow{h\nu} W(CO)_5bpy + CO \qquad (1)$$

$$W(CO)_5bpy \xrightarrow{\Delta} W(CO)_4bpy + CO \qquad (2)$$

The mechanism of the reaction has been clarified by making kinetic measurements over a range of pressures (from 1 atm to 2000 atm) to define the volume profile of the reaction along the reaction coordinate. When Professor van Eldik visited the University of Utah as a consultant in August, 1990, he started Kickel and Brady on some new experiments involving ligands such as 2,9-dimethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline to test the effect of ligand bulk on the thermal ring closure reaction rate (step 2 above). This work is still in progress.

Experiments at the Brookhaven Synchrotron carried out by two graduate students, Stefan Isak and Ben Garland, were designed to clarify the manner in which volatile liquids such as diethyl ether and dichloromethane enhance microphonic photoacoustic signals arising from the illumination of solids such as tin and nickel by a pulsed beam of soft, synchrotron X-rays. Additional experiments were carried out at Utah using visible laser beams in lieu of synchrotron X-rays to achieve the same photoacoustic signals. The arithmetic interpretation of the combined experimental results was finally worked out and a paper submitted for publication (acknowledging DOE support) in June, 1990. It is scheduled to appear in print soon in Applied Physics B.

For many months Stefan Isak had tried to use cresyl violet as a reference compound in his laser photoacoustic measurements of non-radiative quantum yields, ϕ_{NF}, for nonfluorescing dyes such as Evans blue and Trypan blue. Cresyl violet absorbs at the same red wavelengths as these other dyes and is, in principle, a good reference compound because its fluorescence quantum yield, ϕ_F, and its ϕ_{NF} are about equal at 0.5 He discovered in January, 1990 that there is a significant concentration dependence to ϕ_F and ϕ_{NF} for cresyl violet that many recent authors had overlooked. Isak spent several months in 1990 establishing the exact concentration dependence of ϕ_{NF} and ϕ_F for cresyl violet in methanol and is presently using his cresyl violet results to obtain absolute nonradiative quantum yields for Evans blue and Trypan blue in methanol. This work should be ready for submission for publication in January, 1991.

Ben Garland and Daryl Cobranchi, both graduate students, completed experiments designed to measure stability constants for the formation of complex ions between Li^+ and several crown ethers in a low temperature molten salt (55/45 mole % 1-methyl-3-ethylimidazolium chloride to $A\ell Cl_3$). The lithium-crown ether stability constants were found to increase in the order 18-crown-6 < 12-crown-4 < benzo-15-crown-5 < 15-crown-5. The use of low temperature molten salts as the electrolyte medium in lithium batteries and the addition of crown ethers to enhance the conductivity of the electrolyte are both matters of continuing practical interest. The resulting paper was submitted for publication to Inorganic Chemistry in June, 1990. It has been accepted for publication subject to minor revisions.

Personnel

Persons paid from this grant during the progress report period include (in alphabetical order): Bryan Brady, undergraduate; E. M. Eyring, principal investigator; Ben Garland, graduate student; Stefan Isak, graduate student; Bernice Kickel, graduate student; and H. Paul Wang, postdoctoral research associate.

Publications Acknowledging Support of this Grant Since April 1, 1987

1. S. J. Komorowski and E. M. Eyring, "Pulse Shapes of Nanosecond Photoacoustic Signals in Liquids Detected by Piezoelectric Foil", J. Appl. Phys. 62, 3066-3069 (1987).

2. E. M. Eyring, "New Tools for the Study of Surfaces", in Preparative Chemistry Using Supported Reagents, P. Laszlo, Editor, Academic Press, San Diego, CA, 1987, Chapter 7, pp. 115-140.

3. S. J. Komorowski, S. J. Isak, and E. M. Eyring, "Optical Detection of the Pulsed Photoacoustic Signal combined with Thermal Lens Measurement: A Powerful New Tool for Radiationless Relaxation Studies", in Photoacoustic and Photothermal Phenomena, P. Hess and J. Pelzl, Editors, Springer-Verlag, Berlin, 1988, pp. 103, 104.

4. S. J. Komorowski and E. M. Eyring, "Comparison of the Sensitivity and Time Resolution of the PVF_2 Foil and Beam Deflection Detection Methods for Pulsed Photoacoustic Signals in Liquids", in Photoacoustic and Photothermal Phenomena, P. Hess and J. Pelzl, Editors, Springer-Verlag, Berlin, 1988, pp. 484, 485.

5. S. J. Isak, S. J. Komorowski, C. N. Merrow, P. E. Poston, and E. M. Eyring, "Thermal Lens Measurements in Liquids on a Submicrosecond Time Scale", Appl. Spectrosc. 43, 419-422 (1989).

6. 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.

7. D. P. Cobranchi, N. F. Leite, S. J. Isak, S. J. Komorowski, A. Gerhard, and E. M. Eyring, "Pulsed Laser Photothermal Radiometry and Photothermal Beam Deflection Spectroscopy: Determination of Thermal Diffusivities in Liquids", in Conference Proceedings of Photothermal Phenomena, B.S.H. Royce, Editor, Springer-Verlag, New York, in press.

8. 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, in press.

9. B. A. Garland, D. P. Cobranchi, A. Gerhard, Y.-H. Huang and E. M. Eyring, "^{7}Li NMR Determination of Stability Constants for Lithium-Crown Ether Complexes in a Room Temperature Molten Salt", Inorg. Chem., accepted for publication subject to minor revisions.

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