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ULTRA-FAST REACTION RATES IN SOLUTION
RELATED TO ELECTROCHEMISTRY AND
CORROSION

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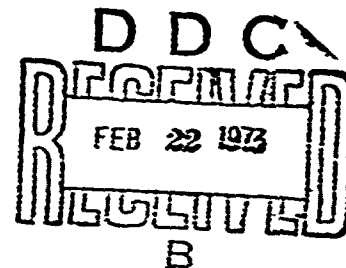
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13. ABSTRACT Report of research progress for the period January 1, 1969 to December 31, 1972, with emphasis on activities during the concluding six months. Experiments with an apparent pulsed x-ray laser are described including the possible observation of Bragg diffraction of x-rays by a gold foil inserted in the x-ray beam. Results of rate studies of the dimerization of several phthalocyanine dyes in solution and of proton-sulfonphthalein anion recombinations are also described. Developing plans for measuring excited state lifetimes of several photographic dye sensitizers are also discussed.		

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Summary

During the last six months of this grant (1 July - 31 December 1972), significant progress was made in three general research areas. The publication in July of our preliminary evidence for a pulsed, "hard" x-ray laser stirred a controversy among laser physicists that still persists. Our own work in the meantime on this problem has been directed toward the development of a theoretical model for our earlier results, an intensified investigation of the characteristic properties of the pumping neodymium: glass laser, and most recently the development of preliminary evidence for Bragg diffraction of the x-ray pulses by a gold foil target.

Our investigations of nearly diffusion controlled reactions in liquid solutions by the electric field jump (E-jump) relaxation technique have also been fruitful during this same period. Our concern is to develop experimental evidence for the precise nature of the rate determining step in reactions between solvated protons and various anions. New kinetic data obtained in water and D₂O provide persuasive evidence for the rate determining step in such reactions being neither diffusion of the ions toward one another nor actual proton transfer but instead reactant re-orientation as by rotation or desolvation. Our simultaneous development of an E-jump apparatus that detects kinetic relaxations at ultraviolet wavelengths promises to provide access to a broad range of rapid carbonium and carbanion reactions in organic solvents.

The third research area in which we have made progress deals with a variety of dyes used in photographic processes. Thermodynamic and kinetic studies of the dimerization of 4, 4', 4'', 4'''-tetraoctadecylsulfonamidophthalocyanine copper (II) and of its Zn²⁺ and VO²⁺ analogs in CCl₄ and

benzene revealed a surprisingly strong dependence of the dimerization equilibrium and rate constants upon the nature of the central metal atom.

Our plans to measure excited state lifetimes for several photographic dye sensitizers were altered by a literature survey that uncovered several previously measured lifetimes of the order of tens of picoseconds. Although we are still assembling a flash calorimeter with an instrument time constant of the order of tens of microseconds that we intend to use in slower rate studies, our present plan is to mode lock a commercial argon ion pumped dye laser to give us access to the picosecond lifetime region apparently characteristic of the important photographic dye sensitizers.

Discussion

The publication in July [J. G. Kepros et al., Proc. Natl. Acad. Sci. U.S., 69, 1744 (1972)] of tentative evidence for a superradiant "hard" x-ray laser coupled with Dr. Kepros' somewhat extravagant claims in the popular press stirred a great deal of interest and controversy in the laser physics community. Dr. Kepros spent the balance of the summer and early autumn working on various theoretical models to account for the observed pulses of x-rays. He also accumulated preliminary experimental data that suggested that other metal ions in sandwich-gelatin targets [such as zinc(II) and iron(III)] produce x-ray pulses when pumped with the Q-switched Nd:glass laser just as well as copper(II) ions can.

In early November, Kepros and E. Eyring attended a Navy sponsored meeting ("New Laser Concepts") in Key Largo, Florida that provided a valuable opportunity to describe the "Utah laser" to some of its sharpest critics. Elton and Andrews of NRL were also present to describe their confirmatory experiments [Appl. Optics, 12, 155 (1975)]. Ben Lax, Art Guenther, Phil Mallozzi and others present with a strong interest in developing x-ray lasers appeared to concede an outside possibility of the Utah experiments being correctly interpreted. The most useful outcome of this conference for the Utah effort was the establishment of an informal collaboration with Dr. Mallozzi on theoretical aspects of the "Utah laser."

In subsequent collaborative sessions in Miami, Fla., and Columbus, Ohio, Mallozzi and Kepros have formulated a model for the Utah laser with the following essential features: in a Nd:glass, Q-switched laser oscillator there can be 10^4 to 10^5 modes sustained by the cavity. These modes

couple in such a way that extremely intense pulses of short duration (from sub-picosecond to tens of picoseconds) with a substantial fraction of the total energy (a joule or more after amplification) are occasionally produced (about one in ten or twenty Q-switched pulses). The energetics of these short pulses interacting with the plasma formed by the main part of the pulse are such that a population inversion is possible.

In mid autumn two students were added to the group working on the x-ray laser: William Herrmann, a B.S. physicist from the University of Texas (Austin) and Dr. J. T. Knudtson, a Columbia University Ph.D. in physical chemistry experienced in the use of high power gas lasers. These two people have spent most of their time mastering the operation of the Nd:glass laser and carrying out minor variations on Kepros' experiment.

Their efforts did not interfere with the execution of what may be Dr. Kepros' most interesting experiment to date. In December, he observed what may be a powder diffraction pattern from a two micron thick gold foil. The pattern was obtained with a Polaroid XR-7 camera system and an intensifier screen and consisted of a series of single spots lying on the circumference of a 5.1 cm diameter circle. The spots were produced by a single pulse from the "Utah laser." The only difficulty with the experiment is that the observed circle of spots does not have the same diameter as that of the principal circle of a powder pattern produced with the same gold foil and camera subjected for several hours to an incoherent beam of Cu K_α radiation from an ordinary x-ray tube. This discrepancy may arise from the physical displacement of the gold foil from its expected position by pressure from the collimator for the calibrating incoherent x-radiation.

The observed single circle of spots in the laser diffraction experiment may be evidence for a single electronic transition in the copper sulfate target emitting coherent radiation. It is unlikely that more than one transition would lase. However, if the emitted beam were merely collimated, polychromatic ($\text{Cu } K_{\alpha_1}$, K_{α_2} , K_{β_1} , and K_{β_2}) x-radiation, pairs (doublets) or quartets of spots would be expected, depending upon the resolving power of the spectrograph, since then the emission would merely depend on a plasma "temperature." The appearance of only a single ring of points is, therefore, preliminary evidence for a true x-ray laser. It would, of course, be more convincing had it been observed with no-screen film instead of Polaroid and had the circles produced by the "coherent" x-radiation and by the incoherent x-radiation been identical in diameter.

At E. Eyring's invitation, Thomas A. Boster of the Lawrence Livermore Laboratories observed the operation of the "Utah laser" on November 2nd. He brought with him three film packs each of which contained three pieces of no-screen film. The packs were apparently made from outer wrappers of Type 57 Polaroid film and were wrapped in 4 mil thick black polyethylene. The Nd:glass laser was fired at over fifty successive copper-gel sandwich targets and the film packs were placed where emitted x-radiation was expected. Boster subsequently developed his films at Livermore and has claimed that all the spots observed on film at Utah are electrostatic in origin.

There are good reasons for doubting Boster's allegation. The spots he reported were obtained with film wrapped in an electrostatic material, polyethylene, rather than aluminum foil routinely used at Utah. Kepros

has since reproduced Boster's spots by wrapping film in Mylar and rubbing it with no exposure to laser radiation. Furthermore, the spots observed in Boster's electrostatic experiments have sharp edges rather than the "feathered" edges observed in the "Utah laser" experiments. This latter type of spot edge would be expected from a pulse consisting of a packet of electromagnetic waves.

The expenses incurred in the above studies were met only in part from this AFOSR grant with the balance of over five thousand dollars coming from awards made to E. Eyring by the University of Utah.

A concurrent effort was made with AFOSR support, during the latter half of 1972, to increase our understanding of so-called diffusion controlled reactions between ions in liquid solutions. A graduate student, David Lentz, and a postdoctoral student, Gary Henderson, collaborated in measuring electric field jump relaxation times for the reaction



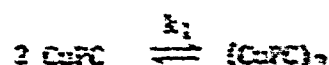
where HIn^- is the protonated form of bromocresol green. As solvents they used water-glycerol mixtures of varying compositions. They determined rate constants at several temperatures between 5° and 60°C and calculated activation parameters that suggest that the rate determining step in the ion-recombination is not diffusion of the ions toward one another but some other process such as rotation of the dianion into a more favorable orientation. However, their experimental data are so imprecise that we have no plans for publication other than in an Appendix to the Ph.D. thesis of David Lentz.

Dr. Henderson left for an industrial job in mid-autumn and his replacement, Dr. Jon Hutchins, in collaboration with Lentz, initiated an E-jump kinetic study of equilibrium (1) for bromocresol green, bromocresol purple, and chlorophenol red in water and in D_2O . The resulting solvent kinetic isotope effect data may be compared with the Debye phenomenological equation for diffusion controlled reactions. In this case, the evidence is much more persuasive that the rate determining step is not translational diffusion of the ions, and a manuscript describing these results has been prepared for publication.

Steven L. Olsen, an electrical engineering undergraduate, during this same six month period designed and began assembling a pulsed ultra-violet light source and faster photomultiplicative detector for the i-jump apparatus that will be used to study reactions involving ultraviolet absorbing species such as carbonium ions and carbanions in organic solvents.

A graduate student, Richard C. Graham, collaborated with Dr. Henderson on a study of equilibria and kinetics of dimerization of several phthalocyanine dyes in non-aqueous solvents. Just previous to the present six month reporting period they had collaborated with Professor Fari Keeley of Brigham Young University in the determination of equilibrium parameters by adiabatic calorimetry. They had determined ΔH° , ΔG° , ΔS° , and ΔV° for the dimerization of 4, 4', 4'', 4'''-tetraoctadecylsulfonamide copper(II) phthalocyanine (hereafter denoted by CuPC) in benzene and CCl₄.

More recently they have used a Durrum-Gibson stopped flow apparatus as a concentration-jump device to determine rate constants for the reaction



in benzene. The temperature dependence of k_1 yields $\Delta H^\ddagger = + 10.1 \text{ kcal/mole}$ and $\Delta S^\ddagger = - 96 \text{ cal/deg.}$

Activation parameters for the dimerization of 4, 4', 4'', 4'''-tetraoctadecylsulfonamide vanadyl(II) phthalocyanine in benzene were also calculated from the temperature dependence of rate constants determined by the concentration-jump method. The calculated values are $\Delta H^\ddagger = + 21.9 \text{ kcal}$ and $\Delta S^\ddagger = - 121 \text{ cal/deg.}$

Ratios of rate constants were not entirely consistent with spectrophotometrically determined equilibrium constants, but it appears possible to account for these discrepancies in terms of a two step reaction mechanism and solvation effects.

The most interesting result of this kinetic study of these two dyes, which were incidentally provided by Dr. Alan R. Monahan of the Xerox Corporation, was the indication that the central metal ion in such large complex ions influences to a surprising extent the rate of the dye dimerization. The results of this dimerization study are found in Graham's Ph.D. thesis and are being prepared for formal publication.

Since his arrival in November, Dr. Knudtson has done a literature survey on excited state lifetimes of photographic dye sensitizers. Polymethine dyes are also useful as saturable absorbers to mode lock lasers. Thus people are able to infer excited state lifetimes from widths of mode-locked laser pulses. For example, 1,1'-diethyl-2,2'-dicarbocyanine iodide has an inferred first excited singlet state lifetime of 3 picoseconds [E. G. Arthurs, et al., Appl. Phys. Lett., 20, 125 (1972)]. A direct measurement of a similar lifetime of 22 ± 4 picoseconds for cryptocyanine was made by Duguay and Hansen [Optics Comm., 1, 254 (1969)]. These results have an important consequence for our proposed investigation of the mechanism of photographic dye sensitization of silver bromide by flash calorimetry [J. B. Callis, et al., Rev. Sci. Instrum., 40, 1599 (1969)]. The flash calorimetric apparatus we have under construction will have, at best, an instrumental time constant of 10 microseconds. We, therefore, intend to use a mode-locked dye laser

as our primary tool for investigating the spectroscopic properties of sensitizing dyes. Such a laser is not presently available commercially, but the techniques for its assembly have been described to us by workers at Bell Laboratories in New Jersey. Only fairly straightforward modifications of the Spectra Physics Model 370 dye laser we have on order will be required.

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* Reprints have been forwarded to AFOSR.