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INTRODUCTION

The effect of hydrostatic pressure P on chemical equilibrium given by the thermodynamic relation

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V}{RT} \tag{1}$$

and the corresponding expression for the effect of pressure on the rate constant k of a reaction in solution

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\ddagger}}{RT} \tag{2}$$

have both been known for a long time.[1] From this latter equation it is apparent that the rate constant of a reaction increases with increasing pressure if $\Delta V^{\ddagger}$, the activation volume, is negative. In other words, if the activated complex, or transition state, has a smaller volume than the initial state, a rise in pressure will speed up the reaction at constant temperature. Moderate pressures ranging up to 100 MPa (1000 atm) are quite adequate for revealing the effect of hydrostatic pressure on rates of reaction in solution.[2]

In the past ten or fifteen years there has been a substantial increase in the number of studies of the effect of pressure on rates and equilibria in solutions arising, at least in part, from the development of convenient new methods for making measurements such as NMR spectroscopy and stopped-flow spectrophotometry at elevated pressures. Several excellent recent surveys cover developments in the high pressure solutior kinetics field up to just a few years ago.[3-6]

There are a number of analytical chemical problems with practical overtones susceptible to investigation by methods involving the use of

moderately elevated pressures. In the present introduction we briefly identify several of these problems that we propose to solve over the next three years at the University of Utah. The methodology of our attack on these problems will be described in subsequent sections of this proposal.

Magnetic resonance imaging (MRI) is a widely used diagnostic tool in modern medicine.[7] Water soluble gadolinium(III) complexes are used increasingly as MRI contrast enhancing agents.[8] Gd(III) chelates have high spin only magnetic moments, labile coordinated water molecules, and undergo slow electronic relaxation making them particularly effective catalysts for the reduction of proton magnetic resonance $T_1$ values of tissue water protons and thus yielding image contrast enhancement. "Relaxivity" $r_1$ is the term assigned to the second order rate constant for catalysis of the longitudinal relaxation of bulk water protons. $r_1$ is obtained from the slope of a $T_1^{-1}$ vs. [Gd complex] plot. Increasing $r_1$ produces greater image contrast enhancement. Since $r_1$ is directly proportional to Q, the number of water molecules solvating the $Gd^{3+}$ ion <u>in</u> the complex, and is inversely proportional to the sixth power of a, the distance between the $Gd^{3+}$ ion and the solvating water molecules, there is interest in knowing how the volume of the gadolinium species changes as $Gd^{3+}(aq)$ ion undergoes complexation by chelating agents such as EDTA and DTPA that are representative of the ligands used to introduce $Gd^{3+}$ safely into an MRI patient.[9]

Radioactive and nonradioactive heavy metals present in the environment can pose serious health hazards. It is possible to trap heavy metals in molecular sieves before they reach potential victims through culinary water.[10] Identification of the symmetry of lattice sites in the molecular sieve at which heavy metal ions adsorb would aid the design of better molecular sieves

for capturing heavy metal ions.

Supercritical fluid chromatography (SFC) has assumed an important role in analytical chemistry as an effective alternative to high performance liquid chromatography (HPLC) for separating certain types of higher molecular weight molecules. While SFC technology is well advanced,[11] there is still much to be learned about fundamental processes occurring in a supercritical fluid solvent such as rates and mechanisms of homogeneous reactions.[12] Ligand substitution reactions like the following thermal ring closure reaction

$$Mo(CO)_5L \rightarrow Mo(CO)_4L + CO \qquad (3)$$

involving a bidentate ligand L do not involve charged reactants or reaction intermediates. Such reactions should therefore be susceptible to study in a supercritical fluid medium such as $CO_2$ or a $CO_2/CH_3CN$ mixture. How the ring closure reaction mechanism is altered by transferring this reaction from the toluene solvent we have previously studied over a range of pressures[13] to a supercritical fluid solvent would be interesting fundamental science that might also suggest new applications for supercritical fluids.

The redox chemistry of porphyrin complexes of metal atoms plays an important role in photosynthesis as well as in oxygen transport in the human circulatory system. How the shape of the porphyrin ring system changes when the complexed metal atom undergoes oxidation or reduction is a matter of continuing interest.[14,15]

RESEARCH PLAN

A. Objectives

In the proposed research we will solve a number of analytical chemical problems with measurement techniques that benefit from the use of elevated hydrostatic pressures. The work will have two major objectives: Production of new insights to interesting chemical problems and refinement of the use of variable pressure methodology in several important chemical measurement techniques.

B. Applications of Elevated Pressure Stopped-Flow Spectrophotometry

If a chemical reaction in the liquid phase is irreversible, i.e. the stability constant K for the formation of products in a reaction

$$A+B \rightleftharpoons C+D; \qquad K=\frac{[C]\,[D]}{[A]\,[B]} \tag{4}$$

is very large, stopped flow spectrophotometry[16,17] (at ambient pressure) is often used to measure the rate constant $k_f$ of the forward reaction. In this method reactants A and B are brought together by two syringes, rapidly mixed, and sent into an observational cuvette. Motion of the mixed liquid is abruptly stopped in the cuvette by the filling of a third syringe, and reaction time constants $\tau$ of a few milliseconds or longer are readily deduced from changes in some property of the mixed liquid such as optical transmittance at a visible or ultraviolet wavelength.

Several workers have constructed stopped-flow spectrophotometers with the sample cuvette, mixer, and three syringes all enclosed in a high pressure cell. A photograph of such an instrument used by the van Eldik group[5] is shown in Fig. 1. A copy of the apparatus depicted in this Figure is presently being constructed in our Chemistry Department machine shop.

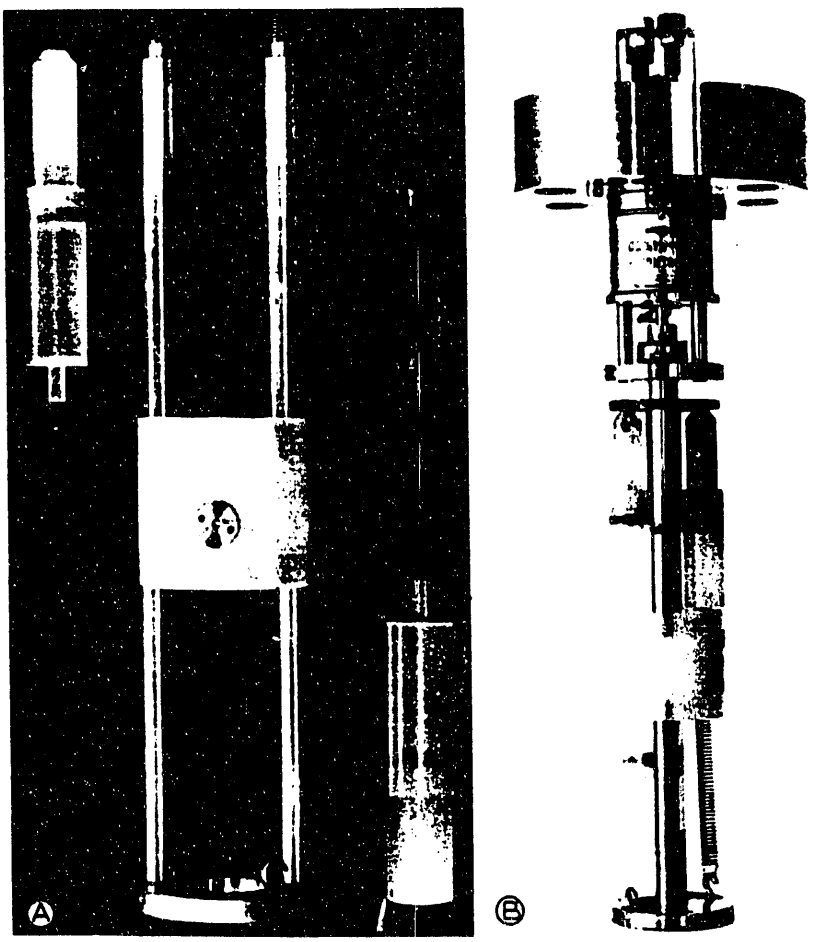


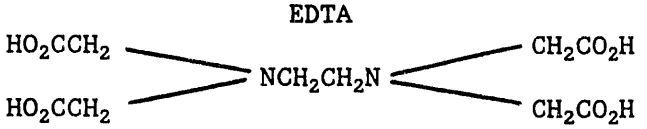
Fig. 1. High pressure stopped-flow apparatus built by the van Eldik research group.[5] The complete unit on the right is approximately 70 cm in length.

Over the years we have published a number of stopped-flow kinetics studies[18-30] using a now obsolete Durrum-Gibson apparatus designed to work only at atmospheric pressure. A variable pressure stopped-flow apparatus permits a determination of $\Delta V^{\ddagger}$ from kinetic data interpreted by eq. 2. The value of $\Delta V^{\ddagger}$ can be combined with equilibrium $\Delta V$ data obtained from spectrophotometric measurements made over a range of pressures at equilibrium and interpreted

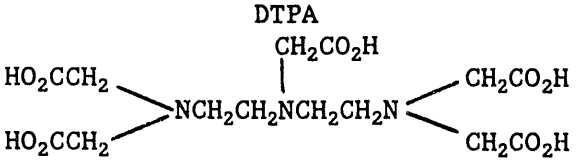
with the aid of eq. 1. The resulting volume reaction profile is analogous to the more familiar plot of energy or enthalpy on the vertical axis and the reaction coordinate plotted along the abscissa. The volume reaction profile is typically a more powerful tool for identifying the mechanism of a reaction occurring in solution than the reaction coordinate profile based on temperature dependence kinetic data.

The reaction of gadolinium(III) ions with a ligand such as ethylenediaminetetracetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA) mentioned in the introduction is just one

EDTA



DTPA



of many moderately rapid reactions in solution whose kinetics can be studied with a high pressure stopped-flow spectrophotometer. Stability constants for the formation of complexes of $Gd^{3+}$ with EDTA and DTPA are very large,[31] $K = [GDL]/[Gd][L] = 10^{17.27}$ and $10^{22.46}$ respectively in 0.1 M ionic strength solution at 25°C. Since most of the toxicity of gadolinium complexes is presumed to arise from release of the highly toxic free $Gd^{3+}$ ion <u>in vivo</u>, it is important that the stability constants for the MRI contrasting agents are high and that the $Gd^{3+}$ ion is not readily displaced from the complex by metal ions such as $Cu^{2+}$ and $Ca^{2+}$ normally present in the body.[31] A high pressure stopped-flow kinetic study of the complexation of $Gd^{3+}$ by DTPA or EDTA will yield insights regarding volume changes in going from an aquo complex to an

encapsulated complex ion of possible interest to users of MRI contrasting agents. The results will certainly be interesting for making comparisons with rates and mechanisms of complexation of other trivalent metal ions by similar polydentate chelating agents.[32]

There are many other reactions susceptible to study with a high pressure stopped-flow spectrophotometer. For instance, the water molecule in the aquo complex $[Ru(L)_5H_2O]^{2+}$ is labile and hence susceptible to ligand substitution and solvent exchange reactions. Recently it has been reported[33] that substitution for $H_2O$ in $[Ru(bpy)_2P(p\text{-}PhX)_3(OH_2)]^{2+}$ by an alkene during oxygenation of alkenes is rate determining and the substitution may occur via a dissociative interchange ($I_d$) mechanism. Thus it would be interesting to study the kinetics of substitution of $H_2O$ by various neutral ligands such as pyridine, imidazole, and thiourea under high pressure using a high pressure stopped flow spectrophotometer to determine volumes of activation and thus to understand the intimate reaction mechanism of ligand substitution and solvent exchange reactions in Ru(II) coordination complexes.

A high pressure stopped-flow spectrophotometer is potentially very useful as a sample mixing device for the extension of our previous high pressure laser flash photolysis experiments to slower time scales. We have reported[13,34] pulsed laser flash photolysis studies of molybdenum carbonyl complexes, $Mo(CO)_6$, in the presence of bidentate ligands L such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and their substituted analogues at pressures up to 150 MPa. The reactions

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO \qquad (5)$$

$$M(CO)_5 + L \rightarrow M(CO)_5L \quad (6)$$

$$M(CO)_5L \underset{\rightarrow}{\overset{\Delta}{\leftarrow}} M(CO)_4L + CO \quad (7)$$

occur sequentially where eq. 7 is called a thermal ring closure reaction. Volumes of activation determined for the thermal ring closure involving several different substituted phens have all been close to zero suggesting an interchange (I) mechanism. When L is bpy, the measured volumes of activation indicate a changeover from an associative interchange ($I_a$) mechanism to a dissociative interchange ($I_d$) mechanism as steric hindrance in the bypy ligand is increased. We propose to continue an investigation now underway of how the volume of activation responds to different substituted bpys when M in the metal hexacarbonyl of eq. 5 is the smaller Cr-metal center and the larger W-metal center. These reactions involving Cr and W are slower than the Mo reactions, i.e. the reaction half-life is usually several seconds for Cr and W. This is slow enough that a high pressure stopped-flow spectrophotometer can be used to mix many successive sample solutions for the laser flash photolysis experiment with only one loading of the mixing syringes and only one pressurization of the syringes and sample cuvette.

A more sophisticated use of the combined high pressure stopped-flow laser flash photolysis experiment would involve the flash photolysis of oxygenated binuclear metalloproteins such as hemerythrin and its monomer, myohemerythrin. Flash photolysis of these complexes results in dissociation of dioxygen from the protein.[35,36] Recombination rates can be studied as a function of pressure to obtain the volumes of activation for the dioxygen binding process ($\Delta V^{\ddagger}_{on}$)at the binuclear iron site of the protein. Since the oxygenation process is a reversible reaction, it is necessary to determine the

volume of activation for the deoxygenation process in order to construct a volume reaction profile for the overall process. The deoxygenation kinetics can be studied in the presence of an oxygen scavenger using the stopped-flow technique. Hence, volumes of activation for the deoxygenation ($\Delta V^{\ddagger}_{off}$) process can be determined using the high pressure stopped-flow spectrometer. The volume profiles thus obtained should suggest an improved mechanistic model of dioxygen binding to non-heme, binuclear iron proteins and should permit comparisons with volume reaction profiles previously reported for the heme site of proteins such as myoglobin[37] and also to ascertain if any major differences exist between hemerythrin and myohemerythrin. Later, such studies could be extended to other binuclear metalloproteins such as hemocyanin.

C. Applications of Elevated Pressure Electron Paramagnetic Resonance (EPR) Spectroscopy

Kuznicki and Hayhurst have invented a new class of inorganic molecular sieves designated as ETS-10 and ETAS-10.[38] These sieves contain silicon, titanium, oxygen and, in the case of ETAS-10, aluminum in the framework structure. These molecular sieves have very large pore sizes on the order of 0.8 nm (ETS-10) and 0.9 nm (ETAS-10). These sieves possess octahedrally coordinated framework sites composed of Ti(IV) bonded with six shared oxygen atoms, resulting in a net negative two charge-per-site. This negative charge is balanced by exchangeable cations. The ETS-10 and ETAS-10 structures have all the traditional properties of classical molecular sieves such as large internal surface area, thermal stability, uniform pore size, and the ability to undergo molecular adsorption and ion-exchange.[39]

The property of these new molecular sieves that is of interest to us here is their unusual capacity for rapidly adsorbing heavy metal ions, such as $Pb^{2+}$, selectively from an aqueous solution containing competing cations such

as $Ca^{2+}$ and $Mg^{2+}$. Consequently, these new sieves have already found a commercial application in a device placed on water faucets for intercepting lead in otherwise potable water.[10]

These new molecular sieves have only been sketchily characterized. For instance, their powder X-ray diffraction properties are known, but the symmetry characteristics of the lattice sites at which particular metal ions adsorb have so far not been reported. We recently completed an EPR study of iron(III) ion-exchanged into ETS-10 and ETAS-10. One of the interesting observations we have reported[40] is the existence of an unusual g = 6.00 EPR signal that we have assigned to a surface site with a possible tetragonal symmetry.

We propose to carry out an EPR study of Gd(III) ion-exchanged into the ETS-10 and ETAS-10 molecular sieves. These studies should help us identify the symmetry of the lattice sites occupied by the Gd(III) cations. Iton and Turkevich[41] reported the EPR spectra of rare earth ions, including Gd(III), exchanged into zeolite-Y. This, and other previous studies, will provide precedents that will aid us in assigning the EPR signals observed for Gd(III) exchanged into ETS-10 and ETAS-10. We will investigate Gd(III) rather than other paramagnetic species such as Eu(II), Cu(II), Mn(II), Co(II), Ni(II) or Ti(III) in our initial EPR studies because of the use of Gd(III) complexes for contrast enhancement in MRI, as noted above. It may be possible using these new molecular sieves to selectively scavenge free Gd(III) ions, resulting from the MRI procedure, from a patient's blood, Knowing more about the cationic sites occupied by Gd(III) in these molecular sieves would then have considerable interest.

In the last few years some researchers have begun to use EPR to

investigate the effects of high pressure on complexation reactions. Sueishi and coworkers[42-44] have used this combination of techniques to learn more about the complexation of nitroxide radicals with cyclodextrins. They were able to obtain stability constants for the complexes and volumes of activation for complex formation.

We will use high pressure EPR techniques to investigate two types of systems: gadolinium complexes in solution and gadolinium ion-exchanged into the ETS-10 and ETAS-10 molecular sieves. With the gadolinium systems in solution we expect to obtain stability constants and volume reaction profile data for such complexes as GdDTPA, GdEDTA, Gd/crown ether complexes and Gd/Schiff base complexes. We would also like to determine what, if any, changes in symmetry occur with increasing applied pressure. Given the importance of associated water for the use of Gd(III) as an MRI contrast agent these studies could provide important information on these complexes in solution.

In the case of the Gd(III) ion-exchanged into the molecular sieves we will investigate the effects of pressure on Gd(III) site occupation. In other words, can one force the Gd(III) to migrate into cationic sites of different symmetry through the application of hydrostatic pressure, and if the migration takes place, is it reversible? With this information one may be able to increase the efficiency of the Gd(III) scavenging process by increasing the number of available sites that the gadolinium cation can occupy.

The EPR spectra will be obtained with a Bruker 200D-SRC X-band spectrometer operating at about 9.5 GHz and 100 kHz field modulation. Samples will be deoxygenated by repeated cycles of evacuation (to $10^{-3}$ torr) and purging with nitrogen. The high pressure EPR sample cell to be used in these

experiments has already been largely built with a copper-beryllium cell body and a quartz capillary sample tube. The design was based on the apparatus reported by Sueishi and coworkers[42] that is shown schematically in Fig. 2.

D. Laser Flash Photolysis Kinetic Studies of $Mo(CO)_6$-2,2'-bipyridine Mixtures in Supercritical Fluid Solvents

A lot of work has already been done with metal complexes in supercritical fluid solvents. For example spectroscopic studies of metal chelates dissolved in supercritical fluids have been reported[45] that were motivated by previous uses of metal chelates in supercritical fluid chromatography.[46,47] Supercritical xenon and $CO_2$ systems have been used in the photochemical synthesis of organometallic species.[48-53] The motivation for measuring the rates of reactions of photogenerated coordinatively unsaturated organometallic species with different ligands lies in the fact that many of these complexes are potential industrial homogeneous catalysts.

Our idea of doing laser flash photolysis studies in a supercritical fluid solution is definitely not new although the particular reaction system we propose below for our flash photolysis study has not been done before. In a recent laser flash photolysis study of benzophenone dissolved in supercritical $CO_2$ Chateauneuf et al.[12] found an apparent increase in the reaction rate constant for the hydrogen abstraction reaction between benzophenone triplet and isopropanol. The bimolecular rate constant increased as the pressure decreased in approaching the critical point. The authors considered three possible explanations for the experimentally observed rate increase: the pressure effect on the reaction rate constant, local composition effects, and cage effects. They concluded that local composition effects were dominant and noted particularly the interesting possibility of

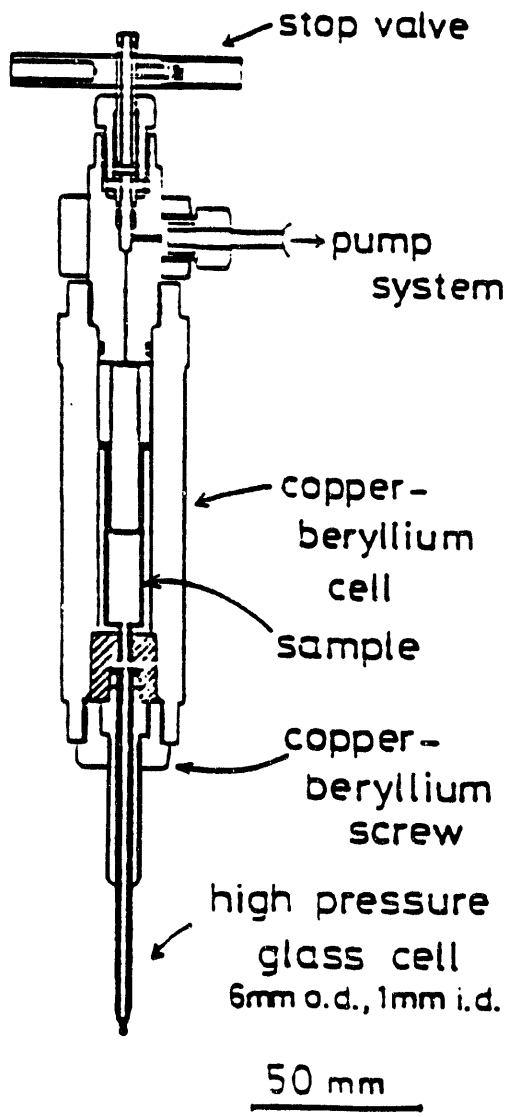



Figure 2. A high pressure cell for use in a standard EPR spectrometer reported by Sueishi et al.[42]

"enhancing reactivity under relatively mild conditions by operation in a supercritical fluid."

We presented above the eqs. 5 through 7 describing the behavior of a molybdenum hexacarbonyl-2,2'-bipyridine sample system in toluene when it is illuminated with a pulse of near ultraviolet ($\lambda$ = 355 nm) laser light.[13] We intend to carry out the same reaction rate studies using supercritical $CO_2$ in place of toluene as the solvent. These experiments can be carried out

conveniently in a high pressure cell connected to a syringe pump which is used to fill the cell with supercritical $CO_2$. The high pressure cell is constructed from stainless steel and has 4 sapphire optical windows. A schematic diagram of our system for making flash photolysis experiments in a supercritical fluid medium is shown in Fig. 3. If the $Mo(CO)_6$-2,2'-bipyridine system in $CO_2$ works as expected, we will also study $Cr(CO)_6$ and $W(CO))_6$ in the presence of bidentate ligands such as 1,10-phenanthroline and 2,2'-bipyridine dissolved in supercritical $CO_2$. Such a combination of sample systems will facilitate the elucidation of the thermal ring closure reaction mechanism in supercritical $CO_2$.

E. Electrochemical Studies of Metalloporphyrins Using Resonance Raman Spectroscopy and High Pressure Techniques

Metalloporphyrins are important in biological processes such as respiration and photosynthesis. The conformation of the porphyrin ring about the metal atom in molecules plays a vital role in the oxidation-reduction chemistry of these systems. Another important property of biomolecules is the manner in which they interact with surfaces. The surface interactions of biomolecules are very specific, and this specificity often serves as an important component of their biological activity.[54]

Surface enhanced resonance Raman spectroscopy can be used to distinguish between different conformations of metalloporphyrins.[55-58] Whether or not the porphyrin ring is planar, cupped or riffled can be detected using normal mode analysis of the Raman spectrum. Because of the structurally specific nature of biochemical interactions, the manner in which the oxidation state of the bound metal changes the conformations of the porphyrin ring is of great interest. We propose to adsorb metalloporphyrins onto a variety of electrode

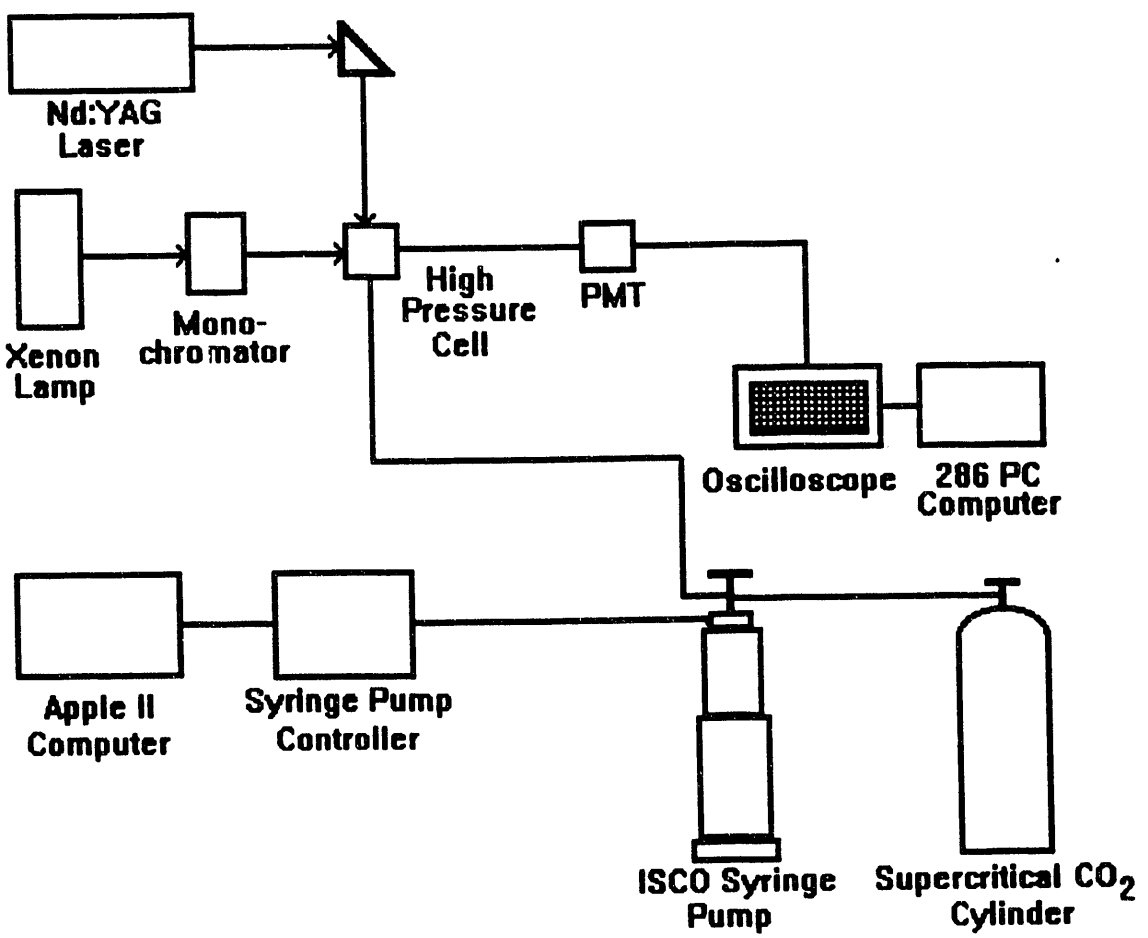



Figure 3. Schematic diagram of sample system arrangement for making flash photolysis rate studies in a supercritical fluid sample system.

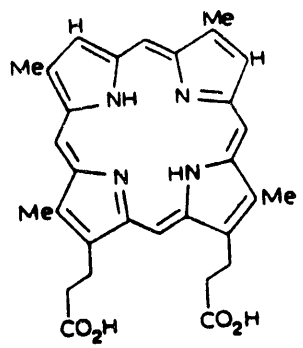
surfaces. Cyclic voltammetry will then be done on these samples with the simultaneous collection of the surface enhanced Raman signal. These Raman spectra will cover a range of 600 to 1800 $cm^{-1}$, with particular attention given to the region of 1400 to 1750 $cm^{-1}$. By simultaneously performing the cyclic voltammetry and monitoring the surface enhanced resonance Raman signal we will be able to explore the structural changes of the porphyrin ring as a

function of the oxidation state of the metal.

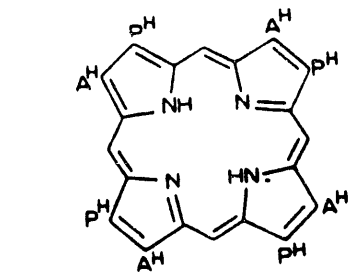
In further experiments we will use modified porphyrins and chemically modified electrode surfaces. These changes will allow us to examine more specific surface interactions. An example would be the comparison of deuteroporphyrin-IX, with two carboxyl groups on one side of the porphyrin ring, and an uroporphyrin-I with its eight carboxyl groups spaced evenly about the perimeter of the porphyrin ring (see diagrams).[59] How much does the surface enhanced resonance Raman signal change between a perpendicular surface interaction, expected for deuteroporphyrin-IX with its carboxyl groups on the same side of the ring and a parallel surface interaction which would be expected in the case of uroporphyrin-I? Studies of this kind should provide valuable insights into the interactions of biomolecules with surfaces. By using chemically modified electrodes an even greater degree of control over surface-adsorbate interactions can be obtained.[60]

In later studies we will carry out similar experiments at elevated pressures (from 10 to 1500 atmospheres). The application of high pressure to protein systems "freezes" them in a given configuration.[61] From Marcus theory[62] it is known that the solvation of a molecule affects its reduction potential. In Marcus theory one of the factors that affects the rate of electron transfer is the outer sphere reorganization energy. This term deals with solvent effects that influence the Gibbs free energy of the electron transfer. In turn the reduction potential of a system can be linked to the Gibbs free energy of the reaction. The application of high pressure to the metalloporphyrin will affect the solvation of the metalloporphyrin and hence its reduction potential. Another factor that would be of interest is the effect that the conformational "freeze" has on the reduction potential of the

# Porphyrins




Deuteroporphyrin-IX




$A^H$ = $CH_2CO_2H$ $P^H$ = $CH_2CH_2CO_2H$

Uroporphyrin-I

metalloporphyrin. Is it more or less difficult to reduce a metalloporphyrin at a given pressure in a given conformation? Again we can follow any changes in the conformation by simultaneously obtaining the surface enhanced resonance Raman signal of the systems. These should help to elucidate the relationship between molecular conformation and reduction potential, and hence, chemical reactivity.

The surface enhanced resonance Raman studies will be done on a computer interfaced SPEX Spectrum One Raman spectrometer equipped with a CCD detector. The lasers to obtain the Raman spectra are a Coherent Innova 300 $Ar^+$ ion laser which will be used to pump a Coherent 890 tunable Ti:sapphire laser. Biomolecular samples can be sensitive to high laser powers, so we will use Raman sample methods that minimize the damage to the sample such as a moving

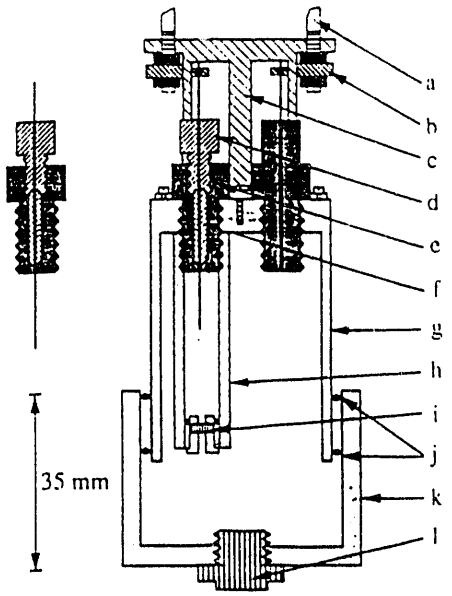



Fig. 4. High-pressure electrochemical cell reported by Sachinidis et al.[63]: $Ag/Ag^+$ reference electrode and Au disk working electrode shown in the cell with an inset of Pt wire auxiliary electrode: (a) bomb electrical terminals; (b) brass connectors; (c) mounting plate; (d) Kel-F backing screw; (e) Kel-F electrode housing; (f) Teflon sleeve (g) upper cell body; (h) reference electrode compartment; (i) internal piston with Vycor glass frit; (j) O-rings; (k) Teflon piston; (l) screw plug.

sample and an unfocussed laser beam. The electrochemistry will be done using an EG&G Princeton Applied Research Potentiostat-Galvanostat Model 273 interfaced to an IBM compatible computer. The high pressure electrochemistry cell will be based upon a recently reported design by Sachinidis and coworkers[63] modified for use with the SPEX Raman spectrometer (Fig. 4). Swaddle and coworkers[64] have also recently published a high pressure electrochemical cell design. The novelty of the experiments we propose to carry out lies in varying the hydrostatic pressure, measuring the Raman spectrum, and cycling the voltage simultaneously.

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BIOGRAPHICAL SKETCH AND PUBLICATIONS OF PRINCIPAL INVESTIGATOR

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Annual Sigma Xi Research Award, 1959 (University of Utah Chapter)
NSF Cooperative Predoctoral Fellowship, 1959-1960
NSF Postdoctoral Fellowship, 1960-61, University of Goettingen
Salt Lake Section ACS: Chairman, 1967
Division of Physical Chemistry, ACS: Member of the Executive Committee 1971 to 1976; Alternate Councilor, 1976 to 1978; Councilor, 1978 to 1984; Secretary-Treasurer, 1986 to 1991.
Utah Award, Salt Lake Section, ACS, February, 1976
1976 NATO Senior Fellowship
Department of the Army Outstanding Civilian Service Medal, 1977
Indo-American Fellowship (for a one month visit to India), 1979
David P. Gardner Research Fellow (of the Univ. of Utah), Autumn, 1980
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EDUCATION:

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| B.A. | Physics, University of Utah, Salt Lake City, UT - 1955 |
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PROFESSIONAL EXPERIENCE:

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| 1973-76, 84-85 | Chairman, Department of Chemistry, University of Utah |
| 1965-68 | Associate Professor, Department of Chemistry, University of Utah |
| 1961-65 | Assistant Professor, Department of Chemistry, University of Utah |
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PROFESSIONAL ORGANIZATIONS:

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Most Recent Publications

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Appendix I: Facilities Available

E.M. Eyring's research group of seven predoctoral students and two postdoctoral coworkers is housed in three research laboratories having a total area of ~1800 square feet in a new (1986) wing of a still quite modern (25 year old) chemistry building. The research group shares a suite of four student offices across the hall from the research laboratories.

The principal tool in these labs to be used in the proposed research is a Quanta Ray DCR-2 Nd:YAG laser and Lambda Physik wavelength tunable dye laser mounted on a Modern Optics 4 ft. x 8 ft. vibration isolation optical table. Adjacent to this table are a LeCroy 9400 oscilloscope interfaced (GPIB) to an IBM-compatible PC (Zenith) and the gadgetry required to develop 150 MPa hydrostatic pressures. The UV-VIS monochromator used in the flash photolysis experiments is a Durrum unit cannibalized from an obsolete stopped-flow spectrophotometer. There is ample bench space in this research laboratory for the new high-pressure stopped-flow spectrophotometer being built in the machine shop.

Items of equipment in Eyring's laboratories that will see some use in the proposed experiments include two Vacuum Atmoshperes Co. glove boxes with inert gas purifier (Dri-Train MO 40-2) and regenerative flow (RFG-1), three additional IBM PC compatible microcomputers, a Hewlett-Packard 8452A diode array UV-VIS spectrophotometer, balances, and two fume hoods.

A departmental Bruker 200D ESR spectrometer to be used in some of the proposed experiments is housed in the research laboratory of Professor Walther Ellis. The EG&G PAR Potentiostat-Galvanostat to be used in the proposed Raman experiments is also in Dr. Ellis' laboratory.

The new departmental Raman spectrometer to be used in some of the proposed experiments is housed in an optical laboratory for all departmental

users located near the Ellis research laboratory.

The departmental research equipment inventory also includes a Cary UV-VIS-NIR spectrophotometer, a Bio Rad (Digilab) FTS-40 FT-IR spectrometer with two optical benches for mid- and far-IR spectral measurements, eight FT-NMR spectrometers, the largest of which is a 500 MHz unit, over 14 major commercial lasers, a high resolution GC-mass spectrometer with FAB capability, and a Syntex P1 Autodiffractometer for X-ray crystallography.

The departmental electronics, machine and glassblowing shops are staffed by a total of ten full-time professionals. The departmental optical, magnetic resonance, X-ray crystallographic, and mass spectral laboratories are managed by five additional full-time professionals including four Ph.D.'s.

The University of Utah has an IBM 3090-600S supercomputer that is available for researchers requiring large disk and RAM resources. The IBM 3090 is housed at the University Supercomputing Institute a short distance away from the Chemistry Building.

The Chemistry Dept. has a SUN 670MP 4 CPU computer that is available for general computation and numerically intensive computation. The Dept. also has a Novell network of IBM PC clones and an Appletalk network of Macintoshes. A DEC microVAX 3100 is used primarily as the mail server and name server but can be used for limited computations. These computers are housed in the Chemistry Building.

# END

# DATE FILMED

12/30/92