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LASER STUDIES OF REACTIONS

by

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→ Research at the University of Utah under ONR contract ~~N00014-75-C-0796~~ covering the period March 1975 - February 1979 * ~~is described~~. (1) Results of ultrasonic absorption kinetics studies of macrocyclic ligands (crown ethers and cyclodextrins) in aqueous salt solutions ~~are described~~ and ~~an~~ application of these results to ~~an~~ a scheme for separating radioactive cesium and strontium from nuclear reactor wastes; ~~is sketched~~. (2) An unsuccessful laser flash photolysis study of bovine rhodopsin; ~~is mentioned~~ (3) The evolution of hydrogen gas from a

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visibly illuminated, water bathed, titanium(III) exchanged zeolite ~~is discussed~~, and the construction of a photoacoustic spectroscopy apparatus for determining the action spectrum of this material. ~~is described.~~ Three recommendations for further work are outlined. The report concludes with a list of sixteen publications acknowledging ONR support.

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Abstract

Research at the University of Utah under ONR contract N00014-75-C-0796 covering the period March 1975 - February 1979 is described. Results of ultrasonic absorption kinetics studies of macrocyclic ligands (crown ethers and cyclodextrins) in aqueous salt solutions are described. An application of these results in a scheme for separating radioactive cesium and strontium from nuclear reactor wastes is sketched. An unsuccessful laser flash photolysis study of bovine rhodopsin is mentioned. The evolution of hydrogen gas from a visibly illuminated, water bathed, titanium(III) exchanged zeolite is discussed, and the construction of a photoacoustic spectroscopy apparatus for determining the action spectrum of this material is described. Three recommendations for further work are outlined. The report concludes with a list of sixteen publications acknowledging ONR support.

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CROWN ETHER REACTION KINETICS

Edward M. Eyring, Michael M. Farrow, Licesio J. Rodriguez, Lindsay B. Lloyd, Ronald P. Rohrbach, and Evan L. Allred.

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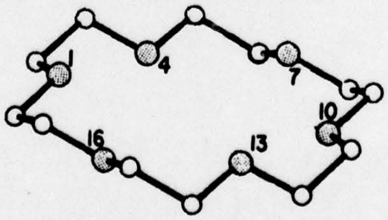
ABSTRACT. The macrocycles 18-crown-6 and 15-crown-5 in aqueous solution undergo at least one rapid conformational change detectable by ultrasound. A correlation between ring size and rigidity of such macrocycles and the rapidity of the conformational change is suggested. A linear inverse correlation exists between the rate constant for formation of crown ether-alkali and alkaline earth metal cation complexes and the charge density of the cation. 2,6-dimethylylbenzoic acid-18-crown-5 does not significantly accelerate cleavage of glycine p-nitrophenyl ester in aqueous solution whereas crown ethers with functionalized side arms do catalyze this type of reaction. Ultrasonic absorption kinetic data are reported for aqueous amino acid-crown ether complexation reactions that indicate the complexation step is unlikely to be rate limiting in any such crown ether catalyzed process in water-like solvents.

It was C. J. Pederesen (1) who coined the name crown ether in 1967 to describe molecules such as 1,4,7,10,13,16-hexaoxacyclooctadecane



This particular macrocycle with eighteen atoms in the ring, six of which are oxygens, is called 18-crown-6. The crown ethers have commanded wide attention because of their capacity for selectively binding cations. Among their many applications the crown ethers were at first viewed (2) only as models of naturally occurring antibiotic facilitators (e.g. valinomycin) of ion transport through biological membranes. However, the crowns have lately assumed potential commercial importance as ion selective carriers through organic liquid membranes designed to separate different (radioactive) isotopes of the same element as well as ions of different elements dissolved in concentrated aqueous media (3,4). Extensively modified crown ethers have also been studied for their potential utility as homogeneous catalysts (5-7). Our own interest in the kinetic properties of crown ethers grew out of these two general applications of crown ethers in other laboratories.

A Joule heating temperature jump (T-jump) relaxation method study (8) of the kinetics of complexation of monovalent cations in methanol by debenzo-30-crown-10 particularly intrigued us. Chock had found the rate of complexation of several monovalent cations (Na^+, K^+, NH_4^+, etc.) to be almost diffusion controlled and essentially too fast for precise determination by T-jump equipment then available to him. He also noted an even faster relaxation process that was completely inaccessible. This latter relaxation process Chock ascribed to a conformational change of the dibenzo-30-crown-10 between two ligand conformers one of which is more suitable for complexing the cation. Such an inference is entirely consistent with known, rapid conformational equilibria in solutions of valinomycin (2), for example.

Valinomycin and dibenzo-30-crown-10 are both large enough macrocycles to envelope a monovalent cation with geometries (9,10) for the backbones of the macrocycles in the complex that have been likened to a deformed bracelet and to the seam on a tennis ball. Smaller crown ethers such as 18-crown-6 can only girdle (11) a monovalent cation, so it is natural to wonder whether a rapid conformational preequilibrium involving so small a crown must precede complexation of the cation. The absence (8) of any systematic trends of complexation rate constants versus cation charge density for dibenzo-30-crown-10 reacting with various monovalent cations in methanol also piqued our curiosity and gave rise to a series of ultrasonic absorption kinetic studies of 18-crown-6 (12-15) and 15-crown-5 (14,16) interacting with a variety of monovalent and divalent cations in aqueous solution. Several conclusions emerge from this work:

1) The small 15-crown-5 and 18-crown-6 rings in aqueous solution undergo a rapid conformational change [analogous to the one inferred by Chock (8) for dibenzo-30-crown-10] with the dominant conformer being the one that complexes the cations.
2) A plot of $\log_{10} k_r$, where k_r is the complexation rate constant, versus (ionic charge/ionic radius) for the ions Na^+, K^+, Rb^+, Cs^+, NH_4^+, Sr^{2+} and Ba^{2+} and the ligands 15-crown-5 and 18-crown-6 in water gives rise to a very satisfactory straight line of negative slope (14).
3) The cations Ag^+, Tl^+, Pb^{2+}, and Hg^{2+} react more rapidly with either ligand in water than do the alkali metal (and alkaline earth metal) cations of corresponding charge density.
4) All the complexation rate constants, k_r, for these cations lie within a factor of ten of an average value of $\sim 2 \times 10\ M^{-1}sec^{-1}$ that is in turn two powers of ten smaller than the diffusion controlled limiting value.
5) Variations in stability constants of 18-crown-6 complexing various cations in water arise principally from significant differences in rate constants for dissociation of the complex ions rather than from k_r.
6) The conformational relaxation times in Table I suggest that a correlation exists between macrocycle rigidity and the speed at which the ring undergoes the conformational change.

Table I. Comparison of Concentration Independent, Ultrasonic Relaxations in Several Dissolved Ring Compounds

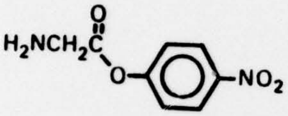
	f_r, MHz	$\tau^{-1}=k_{12}+k_{21}$, sec^{-1}	Ref.
18-crown-6 (aq)	100.7 ± 3.3	6.3×10^8	(15)
15-crown-5 (aq)	22.9 ± 0.4	1.4×10^8	(16)
cyclohexaamylose (aq)	12.3 ± 0.5	7.7×10^7	(17)
dinactin (methanolic)	28	1.8×10^8	(18)
4-methly-1,3-dioxan (in p-xylene)	8	5.0×10^7	(19)

Note that $2\pi f_r = \tau^{-1}$ and that $k_{12} = 6.2 \pm 0.2 \times 10^8$ sec^{-1}, see ref. (15), for the particular case of 18-crown-6 (aq).

The correlation mentioned in conclusion 6) is clearly only a very rough one. For instance, dinactin has three carbon atoms between each pair of ether oxygen atoms in its thirty-two atom ring quite unlike crown ethers that have two methylene groups between neighboring ether oxygen atoms. One also must ignore the presence of four methyl and four ethyl side chains as well as four furan rings in asserting for purposes of this comparison that dinactin approximates (an impossible) 32-crown-8. On the other hand, the bottomless woven basket structure of cyclohexamylose (17) does give rise to a more rigid structure for this ring than one would anticipate for any of the crown or crown-like single chain macrocycles. Ultrasonic techniques should be used to test our speculation that 21-crown-7, 24-crown-8, and dibenzo-30-crown-10 all undergo conformational changes at frequencies exceeding 22.9 MHz whereas the smaller 12-crown-4 ring changes shape with a frequency under 22.9 MHz.

The notion of relative ring flexibility is not easy to make quantitative from theory. However, quantum mechanical calculations of the energies associated with different conformations of such molecules are possible (20,21). The results of such calculations could possibly be correlated with kinetically derived thermodynamic parameters for the conformational change (15). At worst, such an investigation would reveal the importance of solvation effects on the conformational equilibria.

Crown ethers have been modified to render them more effective homogeneous (5-7,22) and heterogeneous catalysts (23,24). Our one preliminary effort in this area was a kinetic study (25) of the accelerated cleavage of glycine p-nitrophenyl ester (I) in the presence of 2,6-dimethylylbenzoate-18-crown-5 (II) in water.



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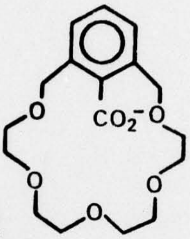

II

The ring of (II) (26,27) should capture and hold the substrate ester (I) while the carboxyl group facilitates the hydrolysis reaction. Extensive examination has shown far less acceleration of the reaction than expected. Thus, for example, an 18-crown-6 to which two thioalkyl sidearms have been added (6) appears to be a much more effective catalyst for ester solvolysis.

The one other useful insight derived form this study (25) of (II) is that the rate of complexation of the ester by the crown ether is probably much too rapid to be rate limiting in any such catalyzed hydrolysis. This we infer from the very rapid rates of complexation of simple amino acids by 18-crown-6 and 15-crown-5 in water shown in Table II.

Table II. Laser Debye-Sears Ultrasonic Rate and Kinetic Equilitrium Constants for Aqueous Amino Acid-Crown Ether Complexation at 25°C.

Amino acid	k_f, $10^7 M^{-1} s^{-1}$	k_r, $10^7 s^{-1}$	K, M^{-1}
	18-Crown-6		
Glycine	8.4 ± 1.0	12.2 ± 1.0	0.7 ± 0.1
α-Alanine	6.1 ± 0.7	5.4 ± 0.8	1.1 ± 0.3
β-Alanine	6.6 ± 0.5	7.2 ± 0.5	0.9 ± 0.1
γ-Aminobutyric acid	5.1 ± 0.2	8.3 ± 0.2	0.6 ± 0.1
Threonine	3.8 ± 1.3	6.0 ± 1.3	0.6 ± 0.4
	15-Crown-5		
Glycine	5.6 ± 0.8	<2	>2

As workers succeed in anchoring crown ether catalysts on surfaces, it will be interesting to see the extent to which catalyzed reaction rates are further enhanced by what is known as a "reduction in dimensionality" (28). The essence of this idea is that a substrate only needs to hunt for an "active site" in two dimensions once it sticks on the catalytic surface. This is in contrast to a longer three dimensional search for the catalyst in the case of homogeneous solutions.

ACKNOWLEDGEMENT. This work was sponsored by a contract from the Office of Naval Research and by Grant AFOSR 77-3255 from the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

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Dismissal of crown ether kinetic studies as pure research of little practical interest is an untenable position. The growing worldwide interest in the Liquid Metal Fast Breeder Reactor (LMFBR) as an alternative energy source to fossil fuels presents a challenging future problem. A means must be found for separating the uranium and plutonium fuel from fission products and the actinides Np, Am, and Cm. Fission products that pose the most serious biological hazards include[1] ^{90}Sr, $t_{1/2}=28.1$ yr; ^{137}Cs, $t_{1/2}=30$ yr; ^{129}I, $t_{1/2}=1.7\times10^{7}$ yr; and ^{99}Tc, $t_{1/2}=2.1\times10^{5}$ yr with ^{90}Sr and ^{137}Cs being the gravest threats. Fusion-fission hybrid reactors could transmute these fission products and activities to less dangerous isotopes (by absorption of fusion neutrons). However, the neutron fluxes required to achieve these transmutations of ^{90}Sr and ^{137}Cs appear impractically high. Fission of the waste actinides by fusion neutrons, on the other hand, does appear to be feasible.[2]

Cooling by forced convection, heavy shielding during transportation, vitrification, and storage in secure underground sites such as salt caverns and holes drilled in the deep ocean sea bed are some of the major steps in the management and disposal of high-level radioactive wastes[3].

An add-on to such a radioactive waste disposal scenario would be the recovery of the ^{90}Sr and ^{137}Cs fission products prior to long term (thousands of years) storage of the residue. There are two arguments for separating out these isotopes: the potential biological hazards associated with the stored wastes decrease more rapidly with time in their absence and these particular strontium and cesium isotopes may have important practical uses if they can be made available economically in sufficiently large quantities.

Strontium-90 radiation has found use in detecting flaws in steel parts[4] and in oceanographic and biomedical applications (e.g. heart pacemakers) as the energy source of milliwatt thermoelectric generators[5]. A 60 W, 40V thermoelectric generator suitable for large lighthouses has also been described[6]. The cesium-137 irradiation of foods to achieve longer shelf-life[7] and of municipal sludge for sanitary reasons[8] may create a demand for this isotope. In 1971, it was projected that future demands (primarily naval applications) for strontium-90 could be met through 1978 by the reprocessing plant at Hanford, Washington[9]. The widespread adoption of these isotopes for use in food processing or municipal sanitation would swiftly invalidate such a modest projection.

The use of crown ethers as carriers in liquid membranes to effect isotope separations has already been demonstrated[10]. R. M. Izatt and coworkers are presently seeking crown ether carriers that will be more suitable for isolating strontium-90 and cesium-137 from radioactive wastes[11]. There is good reason to expect that the formation of metal cation-crown ether complexes or their dissociation will be rate limiting in such liquid membrane separations. Thus an improved understanding of the kinetic properties of crown ethers in aqueous and non-aqueous media could assume critical importance in the development of this new separation technology.

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III. NANOSECOND FLASH PHOTOLYSIS OF RHODOPSIN

We have been interested in nanosecond time scale kinetic processes in frequency doubled Nd:glass laser excited bovine rhodopsin. The rhodopsin is removed from rod outer segments (ROS) of the retina using a detergent. There are indications that the nanosecond time scale dark reactions (detected by light absorbance) of rhodopsin are affected by the choice of detergents as the particular detergent alters the protein moiety of rhodopsin called opsin.[1,2]

The graduate student working on this problem succeeded in preparing the rhodopsin and operating the exciting laser and dye laser for detection but has never obtained reliable kinetic data. A major problem was a damaged Hewlett-Packard oscilloscope that was away an unexpectedly long time (mid-November, 1978 to mid-March, 1979) under repair.

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IV. LIGHT ASSISTED HYDROGEN GAS EVOLUTION FROM WATER

Interest in the chemical conversion of solar energy to a storable form is not new[1]. The photodissociation of water to produce hydrogen gas has, in particular, received considerable recent attention.[2] Several inorganic cations dissolved in water and illuminated with visible or near ultraviolet light give rise to the evolution of hydrogen gas from the water.[3] A report[4] that a monolayer of ruthenium(II) surfactant complexes when illuminated with visible light produced hydrogen gas particularly excited our curiosity. We wondered if a zeolite ("molecular sieve") could adsorb ruthenium ions and produce a water bathed surface that would yield hydrogen when illuminated with visible light. Our experiments with Ru(II) and synthetic zeolites proved disappointing as have more recent experiments in another laboratory[5] in which layers of ruthenium were created in a naturally occuring clay. In neither case was hydrogen gas observed to evolve under visible illumination.

We subsequently succeeded in exchanging titanium(III) ions into zeolite A and observed the evolution of hydrogen gas when the water covered zeolite was exposed to even quite long (red) visible wavelengths[6]. A thermal restoration of the oxidized titanium to the +3 state does not approach completion near enough to make a cyclic hydrogen producing process practical. However, the significant shift in the action spectrum of titanium(III) to longer wavelengths when adsorbed on zeolite A is in itself interesting. Bard[7] has shown that one may use photoacoustic spectroscopy (PAS) to determine the visible action spectrum of similar gas evolving systems. We had had some previous success[8,9] with photoacoustic spectroscopy of solids and therefore decided in autumn, 1978, to construct a microphonic PAS system to determine the action spectrum of titanium(III) exchanged zeolite A.

A differential scheme achieved with a double PAS cell design employing microphones and variable volume resonance cavities[10] seemed most suitable for our intended application. We foresaw the need to significantly enhance vibration isolation, acoustical isolation, signal to noise in the detection, and optical efficiency.

Vibration isolation was improved by placing all components except the mechanical chopper on an optical bench supported by four inches of foam rubber. Light beam chopper vibrations were eliminated by supporting the entire chopper assembly independently on a wall anchored Unistrut/Flexiframe structure. Sound isolation necessitates the elimination of acoustical "leaks" by totally enclosing the PAS cells, creation of acoustical interface mismatches, and acoustical wave dispersion between two hard surfaces. One acoustical mismatch was created by placing one Plexiglas 6"x6"x12" box inside another 10"x10"x16" Plexiglas box. The lowest resonance for the outer box is calculated to be 442 Hz while the lowest for the inner is calculated to be 563 Hz; hence, the boxes tend not to resonate with each other. A second acoustical mismatch is achieved by placing each PAS cell on a tripod of three pointed screws. Acoustical dispersion is fostered by a one inch layer of Fiberglass insulation between the inner and outer box: sound waves transmitted by the outer box are dispersed by the Fiberglass much as a randomly blazed optical grating would disperse light; the power of any specific frequency sound wave is spread over numerous frequencies, and the resultant multitude of low power frequencies are essentially stopped by the mismatches with the hard surface of the inner box. Electrical cables to the PAS cells are left long to avoid passage of resonant frequencies and enter the boxes through O-rings.

Each PAS cell was fitted on one side with the plunger from a ten cc B-D syringe; the other side was filled with high vacuum oil, and fitted with just the rubber tip of a second 10cc plunger. Thus, hydraulics provide the means for adjusting cell resonance. The cell is closed at the top with either a glass or quartz plate, which is sealed with silicone grease to make the cell air tight. The microphones connect to the cell barrel through a narrow Eustachian tube; O-rings are used to make a gas tight seal. The microphones chosen are extremely inexpensive (under \$3), have high gain over a wide frequency range (-65+/-3dB, 50 to 20,000Hz), have low voltage demand (flat response between 2 and 10Vdc), have a low current drain (1mA, maximum), and are readily available from Radio Shack (Archer #270-092, "Electret Condenser Mike Element"). Batteries were used to power the microphones and a pair of photodiodes (Spectronix SPX-1874-1) were used in the optical chopper circuit. The use of battery supplies allowed the entire detection circuit to have as a common reference the ground from a PAR-124A lock-in amplifier with PAR-116 differential amplifier inputs. Most of the components were connected via barrier blocks for ease of attachment and removal. Chopper frequencies are variable from 100 to 500Hz; lower frequencies can be attained if a different chopper motor power supply is used. Higher frequencies will require a more sophisticated mechanical chopper.

As soon as a 500 watt xenon arc lamp that failed in service has been replaced, the action spectrum of titanium(III) exchanged zeolite A will be determined. This PAS study, an esr investigation of titanium(III) exchanged zeolite A and related systems, and the review of crown ether kinetics reproduced above are the only ONR contract research results remaining to be published.

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V. RECOMMENDATIONS FOR FURTHER WORK

A welding technique involving a combination of laser and ultrasonic effects was reported by Dr. M. M. Farrow in this laboratory. There is an apparent strengthening of the common laser weld by the addition of ultrasonic cavitation and cleaning. Materials scientists interested in pursuing the matter further may wish to contact Dr. Farrow (Office Products Division, IBM Corporation, Boulder, Colorado, 80302.)

Someone should measure (by ultrasonics) the complexation of Cs^+ and Sr^{2+} by crown ethers in non-aqueous solvents that are used in solvent membrane extraction processes. The possible usefulness of such data in developing methods of handling liquid metal fast breeder nuclear reactor wastes was noted above.

Many are interested in solar energy conversion schemes involving metal ions[2], but there is still plenty of room in the field for workers using transition metal ion exhcanged zeolites. The possibility of a hydrogen gas from water invention using zeolites has not been ruled out by our work or that of others so far. Based on the already wide use of zeolites in a variety of industrial applications[3] one may expect that most new scientific knowledge of zeolites will eventually have socially important ramifications.

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VI. PUBLICATIONS FROM THIS LABORATORY ACKNOWLEDGING ONR CONTRACT SUPPORT

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VII. ACKNOWLEDGEMENT

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