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CHARGE SEPARATION IN PHOTOREDOX REACTIONS

Technical Progress Report

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ABSTRACT

The structural aspects controlling charge separation in molecular photoionization reactions in organized molecular assemblies involving micelles, reverse micelles and vesicles and in microporous silica gel materials are being studied by optical and electron magnetic resonance techniques including the time domain technique of deuterium electron spin echo modulation (ESEM) and matrix proton electron nuclear double resonance (ENDOR) to measure weak electron-nuclear dipolar interactions. ESEM and matrix ENDOR are particularly well adapted to the study of disordered systems as exemplified by micelles and vesicles. In addition to conventional studies by optical absorption and electron spin resonance, ESEM and matrix ENDOR complement each other and enable independent detection and analysis of extremely weak electron-nuclear dipolar interactions which give structural information often not available by other experimental techniques. The complementarity of using both these techniques greatly strengthens the conclusions reached. Since dipolar interactions are averaged out by molecular tumbling in liquid solutions, their exploitation requires studies in rapidly frozen solutions. A variety of experiments has shown that micellar and vesicular structure is retained in these rapidly frozen solutions. Also, the conformation of x-doxylstearic acid spin probes has been studied as a function of x in cationic and anionic vesicles in liquid solution by detailed simulation of the electron spin resonance lineshapes. The conformation changes with x and with vesicle charge type are the same as independently measured in frozen solutions by variations of the deuterium electron spin echo modulation depth. This shows that embedded photoionizable molecules in frozen vesicle solutions have similar locations and conformations as in liquid vesicle solutions.

The photoionization yields of alkylphenothiazines in micelles and vesicles have been shown to depend on the alkyl chain length and to correlate with relative distances from the surfactant assembly interface measured by deuterium ESEM and matrix proton ENDOR. The trends are opposite, but understood, in micelles versus vesicles because of the higher disorder of the surfactant alkyl chains within micelles. Thus the location and photoyields can be controlled by the alkyl chain length. This has been confirmed by independent measurements on the photoionization of alkyltrimethylbenzidines and (alkoxyphenyl)triphenyl porphyrins in surfactant assemblies. Fine tuning of this location control can be achieved by addition of suitable cosurfactants such as cholesterol.

Nitroxide spin probes have been used to study the degree of water penetration into mixed ionic/nonionic poly(ethylene oxide) micelles by using ESEM methods and selectively deuterated surfactants. Fluorinated micelles formed from ammonium perfluorooctanoate have also been investigated as have polymer-surfactant interactions involving poly(ethylene oxide) and sodium dodecylsulfate micelles. Finally, a new method for obtaining quantitative information about the nitroxide spin probe conformations and the nitroxide moiety location relative to a vesicle-water interface has been developed based on the analysis of ^{31}P modulation from phosphorus located in the surfactant headgroup. These spin probe studies lead to predictions about the photoionization efficiency in such systems.

Most recently, attention has been focused on the photoionization of alkylphenothiazines and other classes of photoionizable molecules mentioned above in microporous materials like silica gels. This has led to systems showing long-lived charge separation **even at room temperature** which is most exciting. In addition, silica gels can be prepared with variable pore

sizes and it has been shown that the photoionization yield and lifetime is dependent on this pore size. Thus, some measure of control of the photoionization process becomes possible in these solid state systems.

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CHARGE SEPARATION IN PHOTOREDOX REACTIONS

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1. Introduction

Light energy is an energy source that is, thus far, only minimally utilized by mankind. The effective utilization of light energy probably depends largely on appropriate conversion and storage methods. Some current goals involve photoredox reactions to generate a fuel from a cheap abundant nonfuel and direct conversion to electricity. Nature's light storage example is the photosynthetic process in the first step of which chlorophyll is photoionized to result in net charge separation. In an artificial system a key requirement is to achieve net charge separation, since efficient photoionization followed by rapid ion recombination is not a route to practical energy storage. In homogeneous solution rapid ion recombination back reactions are difficult to counteract. In photosynthesis the back reaction is largely prevented by sequential electron transfer to several electron acceptors within an organized molecular assembly. However, even though the x-ray diffraction structures of several bacterial photosynthetic reaction centers have been determined, the essential structural features controlling the electron transfer are still incompletely understood. In our current work we are attempting to obtain a better molecular understanding of the structural aspects controlling charge separation in photoredox reactions in organized molecular assemblies such as micelles, vesicles and reverse micelles and in microporous oxide materials which seem to have potential for long-lived charge separation even at room temperature.

Early objectives focused on modifying the surfactant assembly interface to enhance the photoionization efficiency of embedded molecules. Principal

aspects involved modification of the charge of the interface, the charge density, the surfactant structure, the addition of surface-active additives which changed the local water concentration at the interface and the addition of surface-active molecules which complex counterions to change the local ionic strength near the interface. In the past four years we have focused primarily on developing location control of the photoionizable molecules within the surfactant assemblies with respect to the interface and thereby achieving control of the photoionization efficiency. This has been done by developing synthetic methods to add variable length alkyl chains to suitable photoionizable molecules. We have also developed fine tuning of this location control by modifying the penetrability of the surfactant assembly interface with added cosurfactants that modify the interface structure.

In order to monitor that location control is actually achieved in such experiments our approach has been to measure the weak electron-nuclear dipolar interactions between the paramagnetic photoactive molecule ion and magnetic nuclei in the interfacial region. We have shown that this can be done by using a pulsed electron spin resonance (ESR) technique called electron spin echo modulation (ESEM) in which interactions between the unpaired electron on the photoionized paramagnetic molecular ion are measured relative to deuterium nuclei in water at the interface or in other locations. We have previously shown how this electron spin echo modulation approach can be successfully used to deduce the surrounding structure of paramagnetic species in frozen solutions and how it can be used to monitor the location of a photoproduct ion in surfactant assemblies such as micelles and vesicles. Even though this is relatively well documented, it has been further supported by using matrix proton electron nuclear double resonance

(ENDOR) to independently measure the weak electron-nuclear dipolar interactions.

During this report period we have focused on the synthesis and photoionization of a series of alkyltrimethylbenzidines and (alkoxyphenyl)-triphenylporphyrins which further demonstrate that location control via variable length alkyl chains can be achieved and monitored. We have also continued to use stearic acid nitroxide spin probes to study certain aspects of the structure of these surfactant assemblies and how these structural features are related to the photoionization efficiency of solubilized molecules. Initial studies have also focused on the photoionization of alkylphenothiazines in silica gel materials which show long-lived charge separation even at room temperature.

During the past three years of this project 25 papers have been published and 21 conference and seminar presentations have been given in these areas. Citations are given in Sections 6 and 7. Sections 2 to 5 summarize the highlights of these results. This significant progress has been possible in large part to excellent coworkers that have been supported by the DOE grant and some that have brought their own support.

The principal investigator has spent an average of 10 % of the academic year and 100 % of one summer month on this project each year.

2. Photoionization in Micelles and Vesicles

The synthesis of three types of alkylphenothiazines has been developed for this research as shown in Figure 1. The neutral alkylphenothiazines have the greatest variability of alkyl chain length in this series. In addition,

Figure 1. Synthesis of alkylphenothiazines, phenothiazine alkylsulfonates and phenothiazine alkyltrimethylammonium bromides.

we have synthesized negatively and positively charged alkylphenothiazines in which the N-alkyl group is terminated with a negatively charged sulfonate group or with a positively charged trimethylammonium group. The charged group of these alkylphenothiazines serves to anchor the alkyl chain to a charged interface of a micelle or vesicle and affect the location of the photoionizable phenothiazine moiety.

In order to measure the electron-nuclear dipolar interactions by deuterium ESEM or by matrix proton ENDOR it is necessary to work in frozen solutions in which the dipolar interactions are not averaged out as they are in liquid solutions. We have shown in extensive studies over several years that the micellar and vesicular structure is retained in rapidly frozen aqueous solutions. We have recently carried out detailed lineshape simulation studies of x-doxylstearic acids in **liquid** vesicle solutions where the doxyl group containing a nitroxide moiety is located at different positions along the stearic acid chain and have shown that the position of the doxyl group with respect to the interface in positively and negatively charged vesicles shows the **same** quantitative trend in liquid vesicle solutions as it does in frozen vesicle solutions where this was measured by electron spin echo modulation.

These liquid phase ESR lineshape simulations also support the effects of cholesterol addition in frozen vesicle solutions as follows. Electron spin resonance spectra of a series of x-doxylstearic acids, ($x = 5, 7, 10, 12$ and 16) solubilized in anionic dihexadecylphosphate vesicles containing 10, 30 and 50 mole % cholesterol, were analyzed by employing spectral lineshape simulation. The spectra from the vesicle phase are well reproduced by using the microscopic order - macroscopic disorder model of Freed and coworkers with Brownian rotational diffusion. The partial averaging of the magnetic interactions

by local anisotropic motions in the vesicles is quantified mainly by the order parameter, (S) and the rotational diffusion rate perpendicular to the alkyl chain, ($R_{\perp}$). The simulations show that the order parameter decreases with increasing x , suggesting a relatively extended conformation **unlike** the U-shaped, bent conformation of the x -doxylstearic acid alkyl chain found previously from liquid phase ESR lineshape simulations of x -doxylstearic acids in cationic dioctadecyldimethylammonium chloride vesicles. Furthermore, the headgroup region of the vesicle is less ordered in anionic dihexadecylphosphate than in cationic dioctadecyldimethylammonium chloride vesicles. This result in **liquid** vesicle solutions corroborates the same x -doxylstearic conformations found in **frozen** vesicle solutions by deuterium electron spin echo modulation spectroscopy. The effect of cholesterol is found to decrease the observed order parameter for all doxyl positions. This effect is attributed to more water penetration into the vesicle interface arising from the intercalation of the large rigid cholesterol molecule. The effect of cholesterol addition is supported by using 3-doxyl-5 α -cholestane, a spin probe which resembles cholesterol. It is found that the addition of cholesterol up to 50 mole % has little effect on the observed electron spin resonance spectrum of cholestane.

In these frozen solutions the total photoyield can be easily measured by the doubly integrated ESR intensity of the photoproduced radical ion. In general we find that the photoyield trends follow the deuterium modulation depth trends measured by deuterium ESEM. This means that the photoyield is enhanced by a stronger interaction with water at the interface of the surfactant assembly.

New photoionization studies were carried out in reverse micellar systems. Neutral N-alkylphenothiazines (PC_n , $n = 1, 3, 6, 9, 12, 16$) were

solubilized and photoionized in cetyltrimethylammonium bromide (CTAB)-alcohol reverse micelles at 77 K to investigate the optimum photoionization conditions by varying the cosurfactant alcohol, reverse micellar water pool size and pendant alkyl chain length. The photoproduct radicals were identified and quantified by ESR. The relative locations from deuterated water at the interface were monitored by deuterium electron spin echo modulation and matrix proton electron nuclear double resonance. The photoyields and deuterium modulation depths of the PC_n compounds showed a U-shaped trend with increasing pendant alkyl chain length which indicates U-shaped conformations for the longer alkyl chains. The photoyields of the PC_n compounds decrease with the water to surfactant mole ratio and correlate with decreasing deuterium modulation depths which indicate an increasing distance from the phenothiazine moiety to deuterated interface water. The deeper penetration is attributed to a decreased packing density of the interface region of the reverse micelles. This is supported by decreasing matrix proton ENDOR linewidths with increasing water pool size. A change of cosurfactant alcohol from butanol to octanol slightly decreases the photoyield and the deuterium modulation depths. This reflects deeper solubilization and a decreased rate of photoinduced radical conversion.

Positively charged (phenothiazinylalkyl)trimethylammonium bromides (PC_nTAB , $n = 4, 6, 9, 12$) and negatively charged sodium alkylphenothiazinesulfonates (PC_nS , $n = 3, 6, 9, 12$) were also incorporated into anionic aerosol dioctyl (AOT) and cationic cetyltrimethylammonium bromide (CTAB)/hexanol reverse micelles and were photoionized at 77 K. The photoproduct radicals were identified as the alkylphenothiazine radical cation and were quantitated by electron spin resonance spectroscopy.

The relative locations of the phenothiazine moiety relative to the reverse micelle interface with deuterated water were correlated with the photoionization efficiency by deuterium electron spin echo modulation and matrix proton electron nuclear double resonance spectroscopies. PC_nTAB and PC_nS compounds both show the same U-shaped photoyield trends with increasing pendant alkyl chain length of the charged alkylphenothiazines. This is interpreted as alkyl chain bending to locate the phenothiazine moiety more toward the interface with longer alkyl chains. The photoyield decreases monotonically with increasing interior water pool size in anionic AOT reverse micelles and correlates with an increasingly negative interface charge of AOT due to increasing hydration of the sodium counterions. The decrease correlates with a greater distance for electron transfer with increasing water pool size as shown by the deuterium ESEM results. The photoyields and deuterium modulation depths of PC_nTAB and PC_nS compounds in cationic CTAB/hexanol reverse micelles also show a U-shaped trend versus water pool size except for PC_4TAB and PC_3S . This suggests that more chain bending of the charged alkylphenothiazines occurs in cationic CTAB/hexanol reverse micelles than in anionic AOT reverse micelles, perhaps because the surfactant alkyl chain packing is "opened up" by the hexanol cosurfactant. A higher photoyield for the same charged alkylphenothiazine is found in anionic AOT versus cationic CTAB/hexanol reverse micelles. This surprising result indicates that the interface charge is not the dominant aspect controlling the photoionization. Instead a shorter distance of the phenothiazine moiety to the interface water in CTAB/hexanol reverse micelles due to a less ordered interface structure dominates the photoionization efficiency. This shorter distance is indicated by both ESEM

and ENDOR results. This finding in these reverse micelle systems contrasts with that found in normal micelle and in vesicle systems where the effect of the interface charge is the dominant aspect controlling the photoionization.

We have extensively studied the one-photon photoionization of N,N,N',N'-tetramethylbenzidine in micellar and vesicular solutions. This has been extended to alkyltrimethylbenzidines in which the benzidine moiety was functionalized at an N-alkyl position forming the class of neutral asymmetric molecules, N-alkyl,N,N',N'-trimethylbenzidines (C_n TMB). The three step synthesis procedure is shown in Figure 2. C_n TMB molecules with $n = 1 - 16$ have been synthesized.

N-Alkyl,N,N',N'-trimethylbenzidines (C_n TMB, $n = 1, 4, 8, 12, 16$) were photoionized in rapidly frozen reversed micelles composed of sodium bis(2-ethyl-1-hexyl) sulfosuccinate or aerosol dioctyl (AOT) in isooctane with varying mole ratios of water/AOT. The relative photoyields after irradiation with 300 to 400 nm light were measured by electron spin resonance. The photoyield decreased as the mole ratio of water to AOT increased. This was interpreted as a more negative surface charge density at the organic-aqueous interface as increased water more completely solvates the sodium counterions. The higher negative surface charge density forms a higher barrier for the photoelectron to surmount to enter the water pool. Electron spin echo modulation spectroscopy was used to probe the local magnetic nuclear environment of the photoproduct cation radicals in these reversed micelles and indicated that the cation radicals are located near the interface. Secondary radicals due to interaction of the AOT headgroup with photoelectrons were also observed and assigned.

Synthesis of N-Alkyl, N,N',N' trimethylbenzidine

$\text{R}' = (\text{C}_1 \text{ through } \text{C}_{15})$

Figure 2. Synthesis of N-alkyl,N,N',N'-trimethylbenzidines.

N-Alkyl, N,N,'N'-trimethylbenzidines (C_n TMB, $n = 1, 4, 8, 12, 16$) were also photoionized in rapidly frozen anionic, zwitterionic, and cationic vesicles to demonstrate how control of the electron donor location by its alkyl chain length correlates with the photoyield for this new series of molecules. The relative photoyields of the cation radicals were measured by electron spin resonance. Electron spin echo modulation spectroscopy was used to determine the relative location of the photoproduct cation radical with respect to the deuterated aqueous interface. These relative locations were correlated with the photoyields. The photoyield decreased as the C_n TMB alkyl chain length increased. This photoyield trend correlates with deeper penetration of the benzidine moiety as a function of alkyl chain length as measured by deuterium electron spin echo modulation. Evidence for a relatively inefficient photoinduced radical conversion process in vesicular systems with electron donors was also found.

Porphyrins and their derivatives constitute another important class of photoionizable molecules that are potentially useful in artificial photosynthetic systems. This is particularly true because they absorb visible light. In previous studies with porphyrin derivatives, the localization and photoionization of a series of (alkylpyridyl)triphenylporphyrin derivatives were investigated in vesicular systems. One possible disadvantage in using (alkylpyridyl)triphenylporphyrins in surfactant aggregates is that the ionic characteristics of the quaternary nitrogen act to impede much penetration associated with the alkyl chain. In any case with these pyridyl porphyrins no electron spin echo signals could be detected. So a series of less polar (alkoxyphenyl)triphenylporphyrins (C_n OPTPP) were synthesized according to the method in Figure 3.

DMF = dimethylformamide
RT = room temperature

Figure 3. Synthesis of Alkoxyphenyltriphenylporphyrins

Photoinduced electron transfer from (alkoxyphenyl)triphenylporphyrins (C_n OPTPP) to the interface water of anionic aerosol dioctyl (AOT) and cationic cetyltrimethylammonium bromide/alcohol (CTAB/ROH) reverse micelles at 77 K produces paramagnetic (alkoxyphenyl)triphenylporphyrin cation radical (C_n OPTPP⁺). The photoproducted radicals were identified and quantitated with electron spin resonance by measuring the g factor, hyperfine splitting and the doubly integrated spectrum. The photoproducted radical yields were correlated with the deuterium modulation depth of C_n OPTPP⁺ by electron spin echo modulation, which measures changes in the interaction distance of the porphyrin cation headgroup with deuterated water at the reverse micelle interface as a function of the C_n alkyl chain length. The location of the porphyrin cation headgroup relative to interface deuterated water is controlled by the alkyl chain length of C_n OPTPP, the cosurfactant alcohol and the headgroup charge of the surfactant forming the reverse micelle. A longer alkyl chain decreases the photoyield because of increased hydrophobic interaction between C_n OPTPP and the surfactant alkyl chains of the reverse micelles which "pulls" the porphyrin moiety more into the alkane region of the reverse micelles. This is directly monitored by a decreasing deuterium modulation depth with an increasing alkyl chain length of C_n OPTPP. The photoyield also decreases by changing the cosurfactant alcohol of the cationic CTAB/ROH reverse micelles from 1-butanol to 1-octanol due to decreasing hydrophilicity as the alcohol chain length increases which is confirmed by ESEM data on the degree of interface water interaction. Also, the amount of radical conversion of C_n OPTPP⁺ to surfactant alkyl and cosurfactant alcohol radicals decreases from 1-butanol to 1-octanol which decreases the net photoyield. Finally, the cationic interface charge of CTAB/ROH reverse micelles gives a higher photoyield than in anionic AOT reverse micelles which reflects

electron transfer across the interface to achieve net photoionization. This is partly mitigated by a shorter distance of the porphyrin moiety to the interface in AOT versus CTAB/ROH reverse micelles as shown by ESEM data. Note that this contrasts with the results described for the photoionization of charged alkylphenothiazines in these same reverse micelles. This difference seems due to different average penetration depths from the reverse micellar interface for these two different types of photoionizable molecules.

Photoionization of (alkoxyphenyl)triphenylporphyrins (C_n OPTPP) was also studied in dihexadecylphosphate (DHP), dipalmitoylphosphatidylcholine (DPPC) and dioctadecyldimethylammonium chloride (DODAC) frozen vesicle solutions at 77 K. The photoionization occurs via electron transfer from C_n OPTPP to bulk water at the interface of the vesicles. This process results in C_n OPTPP⁺ formation which is characterized and quantitated by electron spin resonance. The cation yield decreases with increasing C_n alkyl chain length of C_n OPTPP due to an increasing interaction distance between the porphyrin headgroup and interface water. This change in interaction distance is directly measured with electron spin echo modulation by measuring the deuterium modulation depth associated with C_n OPTPP⁺ interactions with deuterated water at the interface. The cation yield also decreases from cationic DODAC to neutral DPPC to anionic DHP vesicles because of a charge effect on electron transfer through the interface. Thus, the two photon photoionization of porphyrins in these vesicle systems is very similar to the one photon photoionization of benzidines and phenothiazines with respect to control of the photoionization yields.

The effects of added alcohols on the micellar interface structure and how this affects the photoionization of incorporated tetramethylbenzidine (TMB) were also studied in sodium dodecylsulfate micelles. The alcohols

used in the study were ethanol, propan-2-ol, butan-1-ol and octan-1-ol. Experiments were performed with both the deuterated and protonated analogues of these molecules. The photoyields were determined from double integration of the first derivative electron spin resonance spectra. The location of the TMB cation relative to the micellar interface was determined from the matrix proton electron nuclear double resonance (H-ENDOR) linewidth at 140 K. In general, the TMB radical cation was observed to have a broader H-ENDOR linewidth for samples in which the protonated alcohol was used. This difference increased when longer chained alcohols were used. The results demonstrate that the shorter chain length alcohols are located at the micellar interface, whereas both butan-1-ol and octan-1-ol intercalate deeper into the hydrocarbon interior of the micelle. The photoyield grew with alcohol addition up to 50 mM after which the yield decreased. The maximum yield was obtained in samples with short chain alcohols. These results showed that the yield depended on the degree of disruption of the micelle/water interface. Although hydration of the interface stabilizes the photogenerated cation thus increasing the yield, this effect competes with the disruption of the interfacial region and concomitant decrease of the negative surface charge. The lower negative surface charge helps increase back electron transfer. The results from this H-ENDOR study are consistent with recent work involving electron spin echo modulation spectroscopy, which showed greater water penetration into the micellar interface upon addition of alcohol.

Water soluble polymers can perturb the micellar interface so such systems constitute another method to affect and control the efficiency of electron transfer across the interface. Photoinduced electron transfer from N-alkylphenothiazines (PC_n , $n = 1, 3, 6, 12$ and 16) solubilized in sodium dodecyl sulfate (SDS) micelles interacting with poly(ethylene oxide) (PEO) to interface

D_2O as an electron acceptor is studied with electron spin resonance and electron spin echo modulation. The photoproducted radicals were identified as the N-alkylphenothiazine cation radical and the surfactant alkyl chain radical of SDS. The total photoyield decreased from PC_1 to PC_3 and then increased to PC_{16} . The photoyields increased monotonically with increasing PEO concentration. The photoyields were correlated with the deuterium modulation depth of PC_n^+ with D_2O at the micellar interface as a function of the alkyl chain length of PC_n and the concentration of PEO since the modulation depth measures relative changes in the interaction distance between the phenothiazine moiety and interface D_2O . The photoyield and deuterium modulation depth trends show a good correlation which indicates that the electron transfer from the phenothiazine moiety to interface water is mainly controlled by the distance between them which is controllably varied by the alkyl chain length of the phenothiazine and the intercalation of PEO into the interface region of the SDS micellar headgroup.

Photoreduction of viologens often constitutes the other half of a photoinduced charge separation system. A comprehensive electron magnetic resonance investigation was undertaken on a series of alkylmethylviologens which were solubilized into a D_2O suspension of dipalmitoylphosphatidylcholine vesicles with and without added cholesterol. These samples were photoirradiated at 77 K with ultraviolet light, and the radical yield was determined by electron spin resonance spectroscopy. The location of the photoreduced species was determined by means of both deuterium electron spin echo modulation spectroscopy at 4 K and matrix proton ENDOR spectroscopy at 140 K. The effect of added cholesterol on the photoyield was correlated with the location of the photoreduced radical within the lipid bilayer. Addition of cholesterol disrupts the interfacial region of the vesicles

allowing increased water penetration which serves to enhance the radical yield. As the pendant alkyl chain length is increased, the photoreduction yield increases and deuterium ESEM and matrix proton ENDOR show that the viologen moiety is "pulled" deeper into the bilayer. This is consistent with the interpretation that deeper solubilization decreases the rate of back electron transfer and results in an increased photoreduction yield.

3. Nitroxide Spin Probe Studies of Vesicle/Micelle Structure

The use of x-doxylstearic acid nitroxide spin probes has continued to be important to probe the structure of frozen micellar and vesicular systems. The results can be related to structural aspects controlling the photoionization of embedded molecules in surfactant assemblies.

Electron spin echo modulation of x-doxylstearic acid spin probes (x-DSA, $x = 5, 7, 10, 12$, and 16) in mixed micellar solutions of ionic and nonionic surfactants has been studied as a function of the doxyl position along the alkyl chain of the stearic acid spin probe and of the mixed micellar composition. The mixed micellar systems investigated were sodium dodecylsulfate (SDS) or dodecyltrimethylammonium chloride (DTAC) with hexakis(ethyleneglycol)-monododecyl ether ($C_{12}E_6$), selectively deuterated along the polyethyleneglycol group ($C_{12}D_6$) or along the alkyl chain ($((CD)_{12}E_6$) in H_2O and D_2O . The average probe conformation and probe location in the pure surfactants and in the mixed micelles was determined as a function of the doxyl position, x . Modulation effects due to the interactions of the nitroxide probe with deuterium in D_2O give direct evidence that the hydration is maximized for an equimolar mixture of SDS/ $C_{12}E_6$ mixed micelles. It was also found that the polar headgroups of SDS and DTAC surfactants are located in the ethylene oxide region of the $C_{12}E_6$ surfactant. A comparative analysis of the deuterium

modulation depths, arising from deuteriums located in the alkyl chain or in the ethylene oxide groups of the nonionic surfactant, shows that SDS polar headgroups are located near the surface of the mixed micelle, close to the second ethylene oxide group of $C_{12}E_6$, while DTAC polar headgroups are located deeper inside the mixed micelle at the fifth or sixth ethylene oxide group of the nonionic surfactant. These results provide an explanation at the molecular level of the different thermodynamical behavior found for mixed micelles of anionic-nonionic and cationic-nonionic surfactants.

Nitroxide spin probes have also been used to investigate fluorinated micellar aqueous solutions of ammonium perfluorooctanoate. Three doxylstearic acids with the nitroxide group in different positions on the alkyl chain were used and deuterated water was used to study the deuterium modulation of the electron spin echo signals. The experimental patterns were interpreted by simulated spectra calculated by taking into account both the echo decay and the nuclear modulation. The analysis determines the number of deuterium nuclei in the surroundings of the nitroxide groups and the time constant for the electron spin reorientation causing spectral diffusion and echo decay. From these data we concluded that water molecules belonging to the nitroxide solvation sphere are maintained in the fluorinated micelles and that the long-chain nitroxide probes are tilted in the micelle core in order to occupy regions with better water accessibility. This was greater for 12-DSA than for 5-DSA and 16-DSA. The modulation of the hyperfine couplings of the methyl protons due to their rotational motion seems to be the main mechanism contributing to the echo decay in these fluorinated micelles.

Electron spin resonance linewidths of 5-, 7-, 12-, and 16 -doxylstearic acids and tempo nitroxides versus the concentration of poly(ethyleneoxide)

(PEO) in sodium dodecyl sulfate micelles show different trends. The ESR linewidths of 5-, 7-, and 16-DSA increase with increasing concentration of PEO, which is interpreted as due to increasing viscosity in the environment of the nitroxide spin probe. The tempo and 12-DSA linewidths were independent of the concentration of PEO. The linewidth was largest for 5-DSA and smallest for tempo. The linewidth of x-DSA decreases from 5-DSA to a minimum value for 12-DSA and then increases somewhat for 16-DSA. This is interpreted as bending of the alkyl chain to provide different locations for the nitroxide moiety relative to the micelle interface. The relative distances of the nitroxide moiety of x-DSA from deuterated water at the SDS micelle interface was measured by deuterium electron spin echo modulation. The distances increased from 5-DSA to 12-DSA and then decreased for 16-DSA. The interpretation of the ESR linewidth trend is supported by the deuterium modulation depth trend. The deuterium modulation depths of x-DSA also increase with increasing concentration of PEO. They are largest for 5-DSA, less for 12-DSA and then larger again for 16-DSA. These changes of the ESR linewidths and deuterium modulation depths for x-DSA indicate alkyl chain bending of x-DSA. The alkyl chain of x-DSA is bent near the 12-carbon position which corresponds to the deepest nitroxide location into the hydrocarbon region of SDS micelles. The data also show that the interaction site of PEO with SDS micelles is near the interface region. These data support the structural interpretation of the photoionization results in the SDS/PEO system discussed above.

A new method for more quantitative determination of the location of x-DSA spin probes relative to micelle or vesicle interfaces when the surfactant headgroup contains phosphorus has been developed based on ^{31}P modulation of electron spin echo patterns. x-DSA ($x = 5, 7, 10, 12, 16$)

spin probes in frozen aqueous solutions of zwitterionic DL- α -dipalmitoylphosphatidylcholine (DPPC) vesicles and anionic dihexadecyl phosphate (DHP) vesicles were studied. Modulation effects due to interactions of the nitroxide moiety in the doxyl group of the spin probe with ^{31}P in the surfactant headgroups prove to be an effective method to obtain quantitative information about the conformation of the spin probes and the nitroxide moiety location relative to the vesicle-water interface. The analysis shows that the x-doxylstearic acid spin probes penetrate about 0.51 nm into DHP vesicles and to a lesser extent into DPPC vesicles.

4. Photoionization in Silica Gels

Silica gels are porous materials with a large internal surface area. Also their average pore size can be varied. As such these are interesting and promising solid materials for organizing photoionizable molecules to achieve net charge separation. Our initial studies appear to have opened up a promising new area for investigation.

The photoionization of N,N,N',N'-tetramethylbenzidine (TMB) trapped in sol gel synthesized silica gels and in commercial silica gels of different pore sizes was studied by diffuse reflectance and electron spin resonance spectroscopy. Some ionization of TMB occurs during incorporation into the silica gels. Additional ionization occurs by photoirradiation at 370 nm. The pore size affects the net photoionization yield, but no difference is seen between sol gel synthesized and commercial silica gels. The half life of the photoproduct TMB⁺ ion in silica gel is about 2 h at room temperature, which is an order of magnitude longer than in micelles.

Methylphenothiazine and other N-alkylphenothiazines were introduced into silica gel pores by impregnation and sol-gel synthesis. The alkylphenothiazines were photooxidized at room temperature by 320 nm irradiation to form stable alkylphenothiazine cation radicals detected by electron spin resonance and diffuse reflectance spectroscopies. The silica gel framework is suggested to be the electron acceptor. The photoyield and stability of the methylphenothiazine cation radical depend on the silica gel pore size. In a small pore silica gel the methylphenothiazine cation radical has a larger photoyield and is more stable with a longer lifetime than in a large pore silica gel. Increasing the alkyl chain length up to hexadecyl does not affect the alkylphenothiazine cation photoyield or stability. However, addition of an anionic sulfate group to the alkyl chain of an alkylphenothiazine doubles its photoyield and increases the stability of the photoproduct radical. It is suggested that the mobility of the alkylphenothiazine cation radical in the silica gel pores controls its photoyield and stability. The alkylphenothiazine molecules in a large pore size silica gel are photooxidized more effectively at 77 K than at room temperature. Impregnation and sol-gel synthesis are equally good for introducing alkylphenothiazine molecules into silica gels for efficient photooxidation.

Chloromethanes were added to silica gel of 14 nm pore size with methylphenothiazine (PC_1) trapped in them. The methylphenothiazine was photoionized by 320 nm irradiation by a one photon process to form stable methylphenothiazine cation radical (PC_1^+) which was detected by electron spin resonance. The addition of CCl_4 or $CHCl_3$ increases the net PC_1^+ photoyield when the samples are irradiated at room temperature while CH_2Cl_2 and CH_3Cl have no effect. Thus, $CHCl_3$ and CCl_4 are suggested to act as better electron acceptors **in competition with** the silica gel framework while CH_2Cl_2 and CH_3Cl do not seem to be able to compete with the silica gel framework.

A chloromethane with more Cl atoms has a greater electron affinity which supports this interpretation. No effects of these chloromethanes on the net photoionization yield of PC_1 in silica gels at 77 K were observed, probably due to the immobilization of the chloromethanes at 77 K.

Photoreduction has also been studied in silica gels. Dimethylviologen dichloride ($MV^{2+}(Cl^-)_2$) was introduced into silica gel pores by impregnation or addition to the sol during sol-gel synthesis. The evacuated silica gel samples containing MV^{2+} were reduced by 320 nm irradiation to form a stable dimethylviologen cation radical MV^+ , which was detected by electron spin resonance and diffuse reflectance spectroscopies. The counter anion, chloride, was shown to be the electron donor. The photoyield and stability of the photoproduced MV^+ radical depend on the pore size of the silica gel which ranged from 1.7 to 14 nm. In a large pore silica gel the MV^+ photoyield is larger and the MV^+ cation radical is more stable than in a small pore silica gel. This is the opposite trend to that observed for photoionization. Replacing the two methyl groups of dimethylviologen with butyl and heptyl alkyl chains did not affect the photoyield or stability of the photoproduced viologen cation radical in the silica gels. It is suggested that stability of the photoproduced MV^+ is controlled by its distance from Cl trapped within the pores. The trend of increasing MV^+ stability and photoyield with increasing pore size is due to a larger separation distance between the MV^+ and the Cl trapping site in the larger pores. It was found that the photoyields were about five times greater in impregnated versus sol-gel synthesized samples. Thus impregnation seems to be the optimum method to achieve the most efficient photoreduction. However, for photoionization both impregnation and sol-gel synthesis show comparable yields.

The photoreduction yields of methylviologen and various alkylated homologues were also studied in X, Y and A zeolites at 77 K in the absence of any reducing counteranion. Upon irradiation at 77 K, dehydrated samples turned light blue and a single line ESR spectrum was observed with a g factor identical to that of the methylviologen radical cation. Samples that were not dehydrated produced ESR spectra about 10 % as intense as those that had the water removed. The photoreduction yield was largest in zeolite Y, less in zeolite X which has more cations and hence more crowding in the cages, and very small in zeolite A which has much smaller cages. The electron donor in these systems is believed to be the anionic aluminosilicate framework of the host zeolite.

The photoexcitation of tris(2,2'-bipyridine)ruthenium(II), $\text{Ru}(\text{bpy})_3^{2+}$ leads to electron transfer to a suitable molecular acceptor and has been much studied for light energy storage systems. Formation of $\text{Ru}(\text{bpy})_3^{3+}$ has been demonstrated by flash photolysis and by steady-state optical spectroscopy using Co complexes or persulfonate as electron acceptors. However, $\text{Ru}(\text{bpy})_3^{3+}$ formed by photolysis has not been stabilized in most cases because back electron transfer is rapid and usually exothermic. The present work demonstrates the room temperature stabilization of $\text{Ru}(\text{bpy})_3^{3+}$ in silica gel formed by oxidation with chlorine gas and by photoinduced charge transfer with strong electron acceptors, and its characterization by electron spin resonance. Silica gel was chosen because it can be obtained with various pore sizes and long-lived photoinduced charge separation involving photoionizable aromatic amines has been achieved in silica gel with the yield dependent on the pore size. Stabilization at room temperature is of particular interest for potential light energy storage systems.

The $\text{Ru}(\text{bpy})_3^{3+}$ yield formed by chlorine gas oxidation can be controlled by the silica gel pore size and decreases with increasing pore size. The $\text{Ru}(\text{bpy})_3^{3+}$ yield is one order of magnitude smaller in 14.0 nm pore silica gel compared to 2.5 nm pore silica gel. The $\text{Ru}(\text{bpy})_3^{3+}$ yield gradually decreases by preheating the silica gel to higher temperatures before impregnation with $\text{Ru}(\text{bpy})_3^{2+}$. These results suggest that the oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ with chlorine gas takes place via a silica gel surface mediated reaction and that the direct reaction of adsorbed $\text{Ru}(\text{bpy})_3^{2+}$ with a chlorine molecule in the gas phase is less effective. $\text{Ru}(\text{bpy})_3^{3+}$ can also be stabilized in silica gel by photolysis in the presence of the electron acceptor $\text{S}_2\text{O}_8^{2-}$ (persulfonate ion) with a 50 % yield or tetrachloro-1,4-benzoquinone (*p*-chloranil) with about a 1 % yield.

5. Other Studies

Urea and its derivatives have been used to modify micellar interfaces and we have utilized them for this purpose in earlier studies. As a byproduct we have used ESR to identify various urea radicals formed by gamma-irradiation. Urea, urea- d_4 , 1,3-dimethylurea, 1,3-diethylurea and 1,1',3,3'-tetramethylurea and their solutions in D_2O were γ -irradiated both at room temperature and at 77 K. The product radicals were identified with X-band electron spin resonance, based on the *g*-factor and hyperfine coupling constants. The radicals formed from urea and urea- d_4 were identified as nitrogen-centered and resulted from N-H bond dissociation. The radicals produced from 1,3-dimethylurea, 1,3-diethylurea and 1,1',3,3'-tetramethylurea were identified as carbon-centered and resulted from C-H bond cleavage. The electron spin resonance signals of 1,3-dimethylurea, 1,3-diethylurea and 1,1',3,3'-tetramethylurea are similar in both the powder and D_2O solution. The radicals

observed from 1,3-dimethylurea, 1,3-diethylurea and 1,1',3,3'-tetramethylurea were identified as $\cdot\text{NH-CH}_2$, $\cdot\text{NH-CHCH}_3$, and $\cdot\text{N(CH}_3\text{)(CH}_2\text{)}$, respectively.

The interaction between charged molecular assemblies and their counterions can be modified by encapsulating the counterion by suitable cage compounds. Earlier results have shown that this can affect the photoionization efficiency across the assembly interface. Here we have studied macrobicyclic cage complexation of lithium ion in lithium dodecylsulfate micelles. The small macrobicyclic cage (5, 12,17-trimethyl-1,5,9,12,17-pentaazobicyclo [7.5.5]nonadecane, CESTO), which can selectively encapsulate lithium ions, has been studied in the presence of micellar solutions of 0.037 M lithium dodecylsulfate (LDS). The CESTO cage behaves as a fairly strong base in the first protonation step ($\log K_1 = 11.83$ where K_1 is the equilibrium constant) and exhibits two different behaviors in LDS micellar solutions. Surface tension, electron spin echo modulation, ^7Li NMR and small-angle neutron scattering (SANS) measurements show that the macrocyclic cage at about pH 10.2 behaves as a bulky counterion, while at about pH 12.7 it selectively complexes lithium counterions at the micellar surface. Furthermore, ESEM studies show that CESTO encapsulates lithium ions at the micellar surface by reducing the amount of water at the surfactant polar headgroups. SANS results near pH 12.5 show that LDS molecules form micelles of quasi-spherical shape with an average aggregation number of 90. The effective ionization of the micelles is about 20 %. The addition of CESTO leads to lithium ion complexation with a drastic reduction in the micellar surface charge and in the hydration number. This is accompanied by the growth of the aggregation number and the micelles become more elongated.

The use of two microwave frequencies in electron spin echo experiments can provide redundant data that can reduce possible ambiguity in determining the geometrical parameters in complex systems. An example was investigated for a copper-porphyrin system as follows. Electron spin echo signals from a powder sample of Cu(II)-(alkylthio)tetraazaporphyrin diluted in the corresponding Ni(II) compound were analyzed to determine the structural arrangement around the paramagnetic center. The electron spin echo decay was studied to obtain information on the electron spin relaxation mechanism. This information is of help in elucidating the structure and properties of Langmuir-Blodgett films formed from copper porphyrins. The experiments were run both at X-band (9.8 GHz) and at S-band (2.7 GHz), and the experimental spectra were simulated in the time domain. Two microwave frequencies were used because the additional constraints in fitting data at two frequencies reduces the ambiguity in the determination of the spectral parameters. In addition, S-band ESE was found to be useful to detect the presence of nuclei at longer interaction distances which give such weak echo modulation at X-band that it can't be analyzed.

6. Publications (Copies Appended)

1. Young Soo Kang and Larry Kevan, Electron Spin Resonance, Electron Spin Modulation and Electron Nuclear Double Resonance Studies on the Photoionization of N-Alkylphenothiazines in Cetyltrimethylammonium Bromide/Alcohol Reverse Micelles: Effects of Alkyl Chain Length of Alkylphenothiazines, Reverse Micellar Water Pool Size and Cosurfactant Alcohol, J. Chem. Soc. Faraday Transactions, 89, 1377 - 1382 (1993).
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6. Chris Stenland and Larry Kevan, Electron Spin Resonance and Electron Spin Echo Modulation Studies of the Photoionization of N-Alkyl, N,N',N'-trimethylbenzidines in AOT Reversed Micelles, J. Phys. Chem., 97, 10498 - 10503 (1993).
7. Hugh J.D. McManus, Young Soo Kang and Larry Kevan, Electron Spin Resonance and Proton Matrix Electron Nuclear Double Resonance Studies of N,N,N',N'-Tetramethylbenzidine Photoionization in Sodium Dodecyl Sulfate Micelles: Structural Effects of Added Alcohols, J. Chem. Soc. Faraday Trans., 89, 4085 - 4090 (1993).
8. Young Soo Kang, Hugh J. D. McManus, Kangning Liang and Larry Kevan, Photoinduced Electron Transfer from Alkoxyphenyltriphenylporphyrins to Interface Water of Aerosol Dioctyl and Cetyltrimethylammonium Bromide/Alcohol Reverse Micelles at 77 K, J. Phys. Chem., 98, 1044 - 1048 (1994).

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11. Young Soo Kang and Larry Kevan, Photoinduced Electron Transfer from N-Alkylphenothiazines to Interface Water of Sodium Dodecylsulfate Micelles as a Function of Poly(ethylene oxide) Interaction with the Interface, *J. Phys. Chem.*, 98, 2478 - 2481 (1994).
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14. P. Baglioni, A. Bencini, L. Dei, C. M. C. Gambi, P. Lo Nostro, S. H. Chen, Y. C. Liu, J. Teixeira and L. Kevan, Structure and Aggregation of Lithium Dodecyl Sulphate Micellar Solutions in the Presence of a Macrocyclic Cage, *J. Phys: Condens. Matter*, 6, A369 - A373 (1994).
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23. M. Romanelli, F. Bonosi, V. Kurshev and Larry Kevan, Two-Frequency Electron Spin Envelope Modulation and Electron Spin Echo Decay of Cu(II)-(alkylthio)tetraazaporphyrin Powder, *J. Phys. Chem.*, 99, 12597 - 12602 (1995).
24. Piero Baglioni and Larry Kevan, Methods of Interface Modification of Micelles and How to Monitor by Electron Spin Resonance and Electron Spin Echo Modulation Spectroscopies, *Heterogeneous Chem. Rev.*, 2, 1 -15 (1995).
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7. Conference and Seminar Presentations

1. (DOE-T403) Subpicosecond Electron Solvation Dynamics in Micelles, P. Baglioni, D. Berti, P. Foggi, R. Righini and L. Kevan, 67th Colloid & Surface Science Symposium, Toronto, Canada, June 20 - 23, 1993.
2. (DOE-T404) Electron Spin Resonance, Electron Spin Echo Modulation and Electron Nuclear Double Resonance Studies of the Photoionization of N-Alkyl, N,N',N'-Trimethylbenzidine in Anionic and Cationic Micelles, Chris Stenland and Larry Kevan, 16th International EPR Symposium, Denver, Colorado, July 26 - 29, 1993.
3. (NSF-179)(Welch-T159)(DOE-T405) Applications of Pulsed Electron Spin Resonance to Transition Metal Ions In Microporous Oxides and to Photoredox Reactions in Vesicles and Micelles, Larry Kevan, Physical Chemistry Seminar, University of Houston, Houston, Texas, October 13, 1993.
4. (DOE-T406) Photooxidation of Phenothiazine Derivatives in Silicas of Different Pore Sizes, B. Xiang and L. Kevan, DOE Solar Photochemistry Research Conference, Tahoe City, California, June 5 - 9, 1994.
5. (DOE-T407) Screening of the Micellar Charge by Complexing Counterions With Macrocyclic Ligands: Topology of the Macrocyclic Ligand and Effective Micellar Charge, P. Baglioni, S. H. Chen, L. Kevan and J. Teixeira, ACS Colloid and Surface Science Symposium, Stanford, Calif., June 19 - 22, 1994.
6. (DOE-T408) Electron Spin Resonance Studies of the Photooxidation of Phenothiazine Derivatives In Silicas of Different Pore Sizes, B. Xiang and L. Kevan, 17th International EPR Symposium, Denver, Colorado, July 31 - August 4, 1994.
7. (DOE-T409) X-Band and S-Band Electron Spin Echo Studies of Cu(II)-(alkylthio)tetrazaporphyrin Powder, M. Romanelli, F. Bonosi, G. Ricciardi, F. Lelj, V. Kurshev and L. Kevan, XXVII Congress Ampere on Magnetic Resonance, Kazan, Russia, August 22 - 29, 1994.
8. (DOE-T410) Photoinduced Electron Transfer from Alkoxyphenyltriphenylporphyrins to Interface Water of Dihexadecylphosphate, Dipalmitoylphosphatidylcholine and Dioctadecyldimethylammonium Chloride Vesicles, Y. S. Kang and L. Kevan, European ESR Meeting on Recent Advances, Paris, France, September 5 - 9, 1994.

9. (DOE-T411) Photoinduced Electron Transfer from Alkoxyphenyltriphenylporphyrins to Interface Water of Dihexadecylphosphate, Dipalmitoylphosphatidylcholine and Dioctadecyldimethylammonium Chloride Vesicles, Y. S. Kang and L. Kevan, Puls '94 Meeting, Zakopane, Poland, September 10 - 16, 1994.
10. (NSF-T200)(Welch-T179)(DOE-T412) Pulsed Electron Spin Resonance Studies on Photolytic and Radiolytic Intermediates, L. Kevan, Curie Medal Award Lecture, Polish Association of Radiation Research Conference, Warsaw, Poland, April 6-7, 1995.
11. (DOE-T413) Photoinduced Charge Separation Across Vesicle and Micelle Interfaces and Within Microporous Materials, L. Kevan Seminar, Institute of Physical Chemistry, Warsaw Poland, April 8, 1995.
12. (DOE-T414) Electron Spin Echo Modulation Studies of Doxylstearic Acid Spin Probes in Frozen Vesicle Solutions: Interaction of the Spin Probe with ^{31}P in the Surfactant Headgroups, V. Kurshev and L. Kevan, Sixth Chianti Workshop On Magnetic Resonance, San Miniato, Italy, May 27 - June 2, 1995.
13. (DOE-T415) (NSF-T210) (Welch-T188) Two-Frequency Electron Spin Echo Modulation and Electron Spin Echo Decay of Cu(II)-(Alkylthio)tetraazaporphyrin Powders, M. Romanelli, F. Bonosi, V. Kurshev and L. Kevan, Sixth Chianti Workshop On Magnetic Resonance, San Miniato, Italy, May 27 - June 2, 1995.
14. (DOE-T416) (NSF-T212) (Welch-T189) A study of a Cu(II)-Alkylthioporphyrin through Electron Spin Echo Nuclear Modulation and Decay, M. Romanelli, V. Kurshev and L. Kevan, First NSR Workshop on Advanced EPR Spectroscopy, Nijmegen, The Netherlands, June 1 - 2, 1995.
15. (DOE-T417) Photoinduced Charge Separation Across Vesicle and Reverse Micelle Interfaces and Within Microporous Materials, L. Kevan, Invited Lecture, 19th DOE Solar Photochemistry Conference, Tamiment, Pennsylvania, June 4 - 8, 1995.
16. (DOE-T418) Electron Spin Echo Modulation Studies of Nitroxide Spin Probes with ^{31}P in Vesicle Interfaces, V. Kurshev and L. Kevan, EPR-95, Sydney, Australia, July 13-15, 1995.
17. (DOE-T419) Stabilization of $\text{Ru}(\text{bpy})_3^{2+}$ in Silica Gel By Charge Transfer: ESR Characterization, K. Matsuura and L. Kevan, Japan Conference on Photochemistry, Fukuoka, Japan, October 10-12, 1995.

18. (DOE-T420) ESR Characterization of $\text{Ru}(\text{bpy})_3^{2+}$ In Aqueous Solution Formed By Gamma-Irradiation, K. Matsuura and L. Kevan, 38th Japan Conference on Radiation Chemistry, Kanazawa, Japan, October 17-19, 1995.
19. (DOE-T421) Stabilization of $\text{Ru}(\text{bpy})_3^{2+}$ In Silica Gels By Oxidation with Chlorine Gas, K. Matsuura and L. Kevan, 34th Japan ESR Conference, Matsuyama, Japan, October 31 - November 2, 1995.
20. (NSF-T222) (Welch-T198) (DOE-T422) Applications of Pulsed ESR to Control Heterogeneous Catalytic Activity and Light Energy Storage, L. Kevan, Physical Chemistry Seminar, University of Houston, Houston, Texas, November 8, 1995.
21. (DOE-T423) Stabilization and Electron Spin Resonance Characterization of $\text{Ru}(\text{bpy})_3^{3+}$ in Silica Gel By Chemical Oxidation and Photoinduced Electron Transfer, 19th DOE Solar Photochemistry Research Conference, French Lick, Indiana, June 8 - 12, 1996.

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