CHARGE SEPARATION IN PHOTOREDOX REACTIONS

Progress Report

July, 1990 - October, 1991

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"Charge Separation in Photoredox Reactions"

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Development of the control of the location of electron donors and acceptors relative to micelle and vesicle interfaces has advanced. A comprehensive review of work in this area showing the efficacy of the addition of alkyl chains to electron donors or acceptors has been published. New work has dealt with the photoreduction of alkylmethylviologens in vesicles in which the combined effect of the alkylmethylviologen chain length and the addition of cholesterol to the vesicle system has been assessed. Although the alkyl chain length effect predominately controls the photoreduction yield it is shown that cholesterol addition can tune the magnitude of this effect. A series of neutral alkylphenothiazines has been synthesized and the effect of alkyl chain length in variously charged vesicles on the photoionization efficiency has been evaluated.

A chapter updating the developments of electron spin echo modulation analysis has been prepared. In addition a short review of the use of electron spin echo modulation analysis to study the location of photoproduct radical cations in micelles and vesicles has been written.

Photoionization of electron donors in micellar systems has also been advanced. The effect of the addition of charged electron acceptors on photoionization in micellar systems has been studied. The effect of

urea addition on the micellar interface structure has been studied by x-doxyl stearic acids combined with electron spin echo modulation. The results indicate that urea replaces some water molecules that solvate the hydrophobic chain and polar headgroups of the amphiphile. Alkyl chain length effects on the photoionization of alkylphenothiazines has been studied in anionic and cationic micellar systems and contrasted with vesicle systems.

Reverse micelle systems have considerable potential since they act as intermediate systems between normal micelles and vesicles with respect to the photoionization process. An electron spin echo modulation study of the structure of AOT reverse micelles with n-doxyl stearic acid spin probes has been carried out so as to determine the probe location and conformation in reverse micelles and the amount of water and isooctane penetration into the AOT reverse micellar interface. The results also demonstrate at a molecular level that the reverse micellar structure is retained upon fast freezing. With this background, the photoionization of phenothiazinyl and carbazolyl alkyltrimethylammonium bromides in frozen AOT reverse micellar solutions has been studied. Both the location of the phenothiazine or carbazole group near the micellar interface and the degree of water disorder near the interface are found to affect the efficiency of photoionization for charge separation.

All current funds are anticipated to be spent or encumbered by January 31, 1992.

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2. Publications from July 1990 to October 1991

1. L. Kevan, Developments In Electron Spin Echo Modulation Analysis, In Modern Pulsed and Continuous-Wave Electron Spin Resonance, L. Kevan and M. Bowman, Eds., Wiley: New York, 1990; Chapter 5.
2. L. Kevan, Location Control of Electron Donors and Acceptors In Photoreduced Charge Separation Across Surfactant Interfaces, Intl. Rev. Phys. Chem., 9, 307-328 (1990).
3. L. Kevan, Electron Spin Echo Modulation Analysis of Photoproduced Radical Cation Locations In Micelles and Vesicles, Radiat. Phys. Chem., 37, 629-633 (1991).
4. Chris Stenland and Larry Kevan, Photoionization in Micelles: Addition of Charged Electron Acceptors, Radiat. Phys. Chem., 37, 423-426 (1991).
5. H. Nakamura, P. Baglioni, L. Kevan and T. Matsuo, Photoionization of Phenothiazine and Carbazole Alkyl Trimethylammonium Bromides in Frozen AOT Reversed Micellar Solutions Studied by Electron Spin Echo Modulation and Electron Spin Resonance, J. Phys. Chem., 95, 1480-1484 (1991).
6. P. Baglioni, H. Nakamura and L. Kevan, Electron Spin Echo Study of AOT Reverse Micelles, J. Phys. Chem., 95, 3856-3859 (1991).
7. Masato Sakaguchi and Larry Kevan, Photoreduction of Alkylmethylviologens in Dioctadecyldimethylammonium Chloride Vesicles: Combined Effects of the Alkylmethylviologen Chain Length and the Addition of Cholesterol to Control the Net Photoreduction Yield, J. Phys. Chem., 95, 5996-6000 (1991).
8. P. Baglioni, L. Dei, E. Ferroni, and L. Kevan, Electron Spin Echo Modulation and Electron Spin Resonance Studies of Sodium Dodecylsulfate and Dodecyltrimethylammonium Bromide Micellar Solutions, Prog. Colloid Polym. Sci., 87, 2843-2847 (1991).
9. Young Soo Kang, Piero Baglioni, Hugh J.D. McManus and Larry Kevan, Alkyl Chain Length Effects on the Photoionization of N-Alkylphenothiazines and Sulfonated Alkylphenothiazines in Anionic Alkyl Sulfate and Cationic Alkyltrimethylammonium Bromide Micelles, J. Phys. Chem., 95, 7944-7947 (1991).
10. Peter Bratt, Young Soo Kang, Larry Kevan, Hiroshi Nakamura and Taku Matsuo, Photoionization of Neutral and Positively Charged Alkylphenothiazines in Positive, Neutral and Negatively Charged Vesicles: Effects of the Alkyl Chain Length, J. Phys. Chem., 95, 6399-6402 (1991).

3. Seminar and Conference Presentations - July 1990 to October 1991
1. Contribution of Continuous and Pulsed Electron Spin Resonance to the Study of the Structure of the Interface of Sodium Dodecylsulfate and Dodecyltrimethylammonium Bromide Micellar Solutions with Added Urea, P. Baglioni, L. Dei, E. Ferroni and L. Kevan, 11th IUPAC Conference on Chemical Thermodynamics, Como, Italy, August 26-31, 1990.
2. Electron Spin Echo Modulation and Electron Spin Resonance Studies of the Effects of Urea Addition to Micellar Solutions, P. Baglioni, L. Dei, E. Ferroni and L. Kevan, Fourth Conference on Trends in Colloid and Interface Science, Catanzaro, Italy, September 24-27, 1990.
3. Electron Spin Echo Modulation and Electron Spin Resonance Studies of Anionic and Cationic Micellar Solutions: Effect of Urea Addition, P. Baglioni, L. Dei, E. Ferroni and L. Kevan, XXIV National Congress on Chemical Physics, Potenza, Italy, October 8-12, 1990.
4. Electron Spin Echo Spectroscopy, L. Kevan, Invited Lecturer, Bat-Sheva Workshop on New Developments and Applications in NMR and ESR Spectroscopy, Israel, October 14-24, 1990.
5. Two Pulse Electron Spin Echo Modulation, L. Kevan, Invited Lecturer, Bat-Sheva Workshop on New Developments and Applications in NMR and ESR Spectroscopy, Israel, October 14-24, 1990.
6. Three Pulse Electron Spin Echo Modulation, L. Kevan, Invited Lecturer, Bat-Sheva Workshop on New Developments and Applications in NMR and ESR Spectroscopy, Israel, October 14-24, 1990.
7. Applications of Electron Spin Echo Spectroscopy to Location Control of Electron Donors In Photoinduced Charge Separation Across Vesicle, Micelle and Reverse Micelle Interfaces, Invited Lecture, L. Kevan, 4th Chianti Workshop on Magnetic Resonance, San Minato, Italy, June 2-8, 1991.
8. Continuous and Pulsed-Wave ESR of Langmuir-Blodgett Films of Doxyl Steric Acid/Stearic Acid, F. Bonosi, L. Kevan, G. Martini and M. Romanelli, 4th Chianti Workshop on Magnetic Resonance, San Minato, Italy, June 2-8, 1991.

9. Electron Spin Echo Modulation Study of Mixed Micelles of SDS, DTAC and Polyethylene Oxide Surfactants, P. Baglioni, E. Rivara-Minten and L. Kevan, American Chemical Society Colloid and Surface Chemistry Summer Symposium, Norman, Oklahoma, June 17-21, 1991.
10. Photoionization Near Vesicle, Micelle and Reverse Micelle Interfaces, L. Kevan, Invited Lecture, 9th International Congress on Radiation Research, Toronto, Canada, July 7-12, 1991.
11. Applications of Electron Spin Echo Spectroscopy to Location Control of Electron Donors in Photoinduced Charge Separation Across Vesicle, Micelle and Reverse Micelle Interfaces, Invited Lecture, L. Kevan, Oji International Conference on Spin Chemistry, Tomakomai, Japan, July 15-18, 1991.
12. Photoionization of Neutral and Positively Charged Alkylphenothiazines in Positive, Neutral and Negatively Charged Vesicles: Effects of the Alkyl Chain Length, P. Bratt, Y.S. Kang and L. Kevan, 14th International EPR Symposium, Denver, Colorado, July 29 - August 1, 1991.
13. Photoreduction of Alkylmethylviologens in Vesicle Solution: Combined Effects of the Alkyl Chain Length in Alkylmethylviologen and the Addition of Cholesterol, M. Sakaguchi and L. Kevan, 44th Meeting of Colloid and Surface Science, Saitama University, Urawa, Japan, September 27-29, 1991.

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