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TECHNICAL PROGRESS REPORT

Project Title:

PHOTOREACTIONS IN MICROSCOPIC REACTIONS:

NOVEL METHODS FOR THE UTILIZATION OF MAGNETIC

EFFECTS ON CHEMICAL REACTIVITY AND ISOTOPE SEPARATION

Principal Investigator: Dr. Nicholas J. Turro

Period of Time Report Covers: January 1, 1990 - September 30, 1990

Award No.: DE-FG02-87ER13653

BETH H. ISRAEL
ASSOCIATE DIRECTOR
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Technical Progress Report
for the Department of Energy

Research Performed During the Budget Year
(January 1, 1990 to August 31, 1990)

General Comments: The Principal Investigator will receive the 1991 Award in Photochemistry from the Inter-American Photochemical Society. He presented plenary lectures on DOE supported research at the American Chemical Society National Meeting (Washington, D. C., August 1990), at the Solar Energy Conversion and Storage Conference (Palermo, Italy, July, 1990), at the Organic Reaction Mechanisms Conference, (Boulder, CO, June1990), at the Reactions in Solution Conference (Canterbury, U. K., July, 1990). He also presented seminars at Unilever Research Laboratories (Edgewater NJ, August 1990), Ciba-Geigy Research Laboratory (Ardsley, NY, June, 1990), at the at the University of Florence, Italy (July, 1990), Bowling Green University (Bowling Green, OH, March, 1990), Penn State University (State College PA, April, 1990), Rutgers University (New Brunswick, NJ, February, 1990) and at the University of Oklahoma (Norman, May, 1990).

He serves as co-chairman of the Board of Chemical Sciences and Technology of the National Academy of Sciences, and is a member of the Editorial Boards of the following journals: Journal of Photochemistry, Journal of the American Chemical Society, Journal of Reactive Intermediates, Langmuir, Spectroscopy Letters and Nouveau Journal de Chemie.

Description of Recent Research Accomplishments

In 1990, DOE supported research has resulted in publications describing the combined effect of isotopic substitution, temperature and magnetic field on the lifetimes of triplets biradicals[1], the structure of the adsorbed layer of dodecylsulfate at the alumina-water interface[2], the synthesis of ^{13}C and ^{2}H-labelled cyclanones to serve as models for the magnetic isotope effect[3], the prospects for

physical organic photochemistry in the 1990's[4], and the role of electron exchange in the electron spin polarization of radicals[5].

The lifetimes for decay of the triplet biradical derived from 2-phenylcycloalkanones were measured by nanosecond transient absorption spectroscopy and served as a probe of the contribution of intersystem crossing and chain dynamics of the intermediate biradicals.[1] The magnetic isotope effect on the biradical lifetime and the temperature dependence of quenching of the biradical by transition metals support chain dynamics as the rate-limiting step at -85°C and intersystem crossing as the rate-limiting step at room temperature. However, the magnetic field effect on the biradical lifetime reaches a maximum around -50°C and persists even a -99°C, in contrast to the magnetic isotope effect and transition metal quenching, which are absent at low temperature.

Fluorescence and electron spin resonance probes were employed to investigate the solid-water interfacial layer formed by dodecylsulfate adsorbed on alumina[2]. The results showed that there were four regions of surface aggregation by the surfactants to form hemimicelles. It was concluded that the hemimicelles are considerably more viscous at the microscopic level than corresponding micelles and that the surfactants in the hemimicelles are more tightly packed near the solid surface than at the air-water interface.

The syntheses of 13-C labelled and perdeuterated derivative of 2-phenyl cyclododecanones, as precursors of flexible triplet biradicals, was described[3].

Current Research Activities

Current investigations include the experimental and theoretical analysis of the efficiency of the 13-C magentic isotope effect as a function of magnetic field. From a theoretical simulation of the results, the parameters responsible for the limiting features of the efficiency can be identified and improved. A wavelength dependence of the efficiency of the magnetic isotope effect has been discovered and will be analyzed in terms of our current model of the mechanism of the magentic isotope effect. A system possible of

expressing a 33-S magnetic isotope effect is being constructed. Several photochemical systems are being explored as candidates for this system.

Systems are being designed that will display various aspects of the magnetic isotope effect in real time. These include time-resolved electron polarization and time-resolved nuclear polarization experiments.

Summary

The approach taken in this research of isotope separation combines a number of disciplines and a battery of modern techniques: mechanistic organic photochemistry, magnetic effects on chemical reactions, the influence of restricted space on diffusion and rotational motion, time-resolved magnetic resonance spectroscopy, time-resolved laser spectroscopy, etc. It has been demonstrated that the breadth of the ideas and techniques provide an intellectual and scientific base to generate new methods and processes which, not only expand and clarify our understanding of the separation of isotopes by magnetic interactions at the microscopic level, but also enrich our understanding of reactive intermediates and the nature of catalytic processes.

References

1. J.-F. Wang, V. P. Rao, C. Doubleday, Jr., and N.J. Turro, "Combined Effect of Isotopic Substitution, Temperature, and Magnetic Field on the Lifetimes of Triplet Biradicals," **J. Phys. Chem.**, *94*, 1144 (1990).
2. P. Somasundaran, P. Chandar, N.J. Turro and K.C. Waterman, "Investigations into the Structure of the Adsorbed Layer of Dodecylsulfate at the Alumina-Water Interface," in **Surfactants in Solution**, vol. 9, K.L. Mittal, ed., Plenum Publishing Corp., 1989, pg. 339.
3. V.P. Rao, J.-F. Wang, N.J. Turro and C. Doubleday, Jr., "Synthesis of 13C and 2H-Labelled 2-Phenylcyclododecanones," **J. Labelled Compds. and Radiopharm.**, *XXVIII*, 193 (1990).

4. N.J. Turro, "Physical Organic Photochemistry," **J. Photochem. Photobiol., A: Chemistry,** *51*, 63 (1990).

5. W.S. Jenks and N.J. Turro, "Exchange Effects and CIDEP", **Res. on Chem. Intermed.**, *13*, 237 (1990).

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