A Supramolecular Approach to the Mechanisms of Photomineralization of Hazardous Materials

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Supramolecular photochemistry provides experimental tools and mechanistic concepts pertinent to the examination of the fate of Air Force chemicals and how they may be photochemically transformed into environmentally benign substances. This benefication process of converting AF chemicals to environmentally benign materials is termed mineralization. A "biomimetic" strategy is adopted for which the laboratory model of benefication is based on processes occurring in nature. This biomimetic model provided us with the strategy of employing supramolecular photo systems to achieve the mineralization of AF chemicals via photosensitized degradation.
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II. Accomplishments/New Findings  During the first year of the project progress was made in two areas: (1) the mechanism of photodegradation of quadricyclane, and (2) the mechanism of photodegradation of high performance fluorocarbon polymers. In area (1) we studied the ESR of photosensitizers capable of reducing and oxidizing quadricyclane as a key first step in its degradation. The mechanistic concepts which drove these studies are that initial acceptance of an electron by quadricyclane or removal of an electron from quadricyclane initiates degradation. We were successful in detecting the ESR signal of the hydrated electron (e$_{aq}^-$), a powerful reducing agent. A paper was published in the Journal of the American Chemical Society.

Additionally, we have produced the radical cation of quadricyclane by alternate synthesis through the photosensitized loss of nitrogen from cyclic azoalkane derivatives. Through the use of chemically induced dynamic nuclear polarization (CIDNP) we have detected the radical cation of quadricyclane and its conversion to norbornadiene radical cation. A paper on the initial phases of this project has been published in the Journal of the American Chemical Society.

In area (2) we have demonstrated that the photosensitized decomposition of fluorocarbons can be readily achieved. As a model substrate, perfluorodecalin was investigated and found to be readily converted to 9,10-unsaturated olefin and the photosensitizer employed. In this project we attempted to convert the olefin to the completely
defluorinated aromatic compound. From this model system, we investigated the photosensitized decomposition of samples of perfluoropolyalkylether sent to us by Dr. L. Gschwender from Wright Laboratory at Wright-Patterson Air Force Base, Ohio. These perfluoropoly-alkylethers are representative of spilled materials studies used in gas turbine engine oils. This work has been published in *Tetrahedron Letters*.

III. Cumulative List of Publications:


IV. Personnel Supported
Dr. Igor Khudyakov
Dr. Nikolaos Kaprinidis

V. Coupling Activities
Dr. Susan E. Burns, a postdoc of Prof. John Hassett of SUNY, Syracuse visited the PI's Laboratories on 4/29/95 to discuss the AFOSR project.
Lois Gschwender from Wright-Patterson AFB, OH sent us two samples of perfluoropolyalkylether for chemical/biochemical fate of spilled material studies used in gas turbine engine oils. The photosensitized decomposition of these materials was investigated.

Dr. Nikolaos Kaprinidis (post-doc in the PIs Laboratories) attended a Joint USAF/Army Contractor/Grantee Meeting on 6/8 and 6/9 1995 in Boulder, CO and presented a paper on "Photochemical Effects on Fate and Transport of Hazardous Aerospace Materials".

New Discoveries, Inventions, or Patent Disclosures: None

Honors/Awards: Distinguished Alumnus Award, California Institute of Technology, May 1996.