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ENERGY STORING ORGANIC PHOTOREACTIONS.(U)
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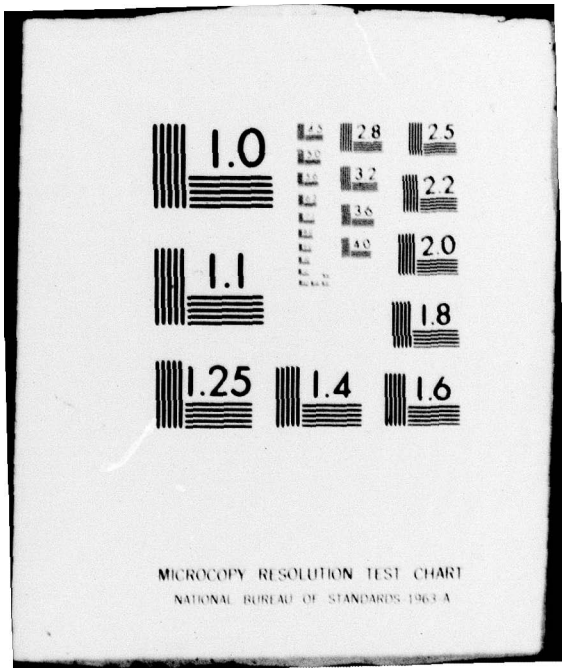
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Results of a study of energy storing organic photoreactions are summarized. Discussion includes criteria for efficient photon energy storage, quantum yield and other quantitative results for a variety of photoisomerization and and photoaddition reactions, the nature of intermediates for these photoreactions, photochemistry of charge-transfer complexes, and prospects for photochemical storage of solar energy.

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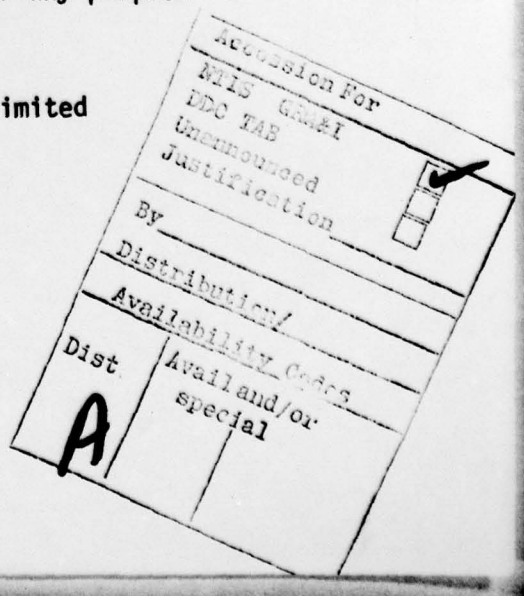

ENERGY STORING ORGANIC PHOTOREACTIONS

INTRODUCTION

The present research program began November 1, 1975 as an outgrowth of studies supported by the Defense Advanced Research Projects Agency (5/1/74 - 10/31/75, monitored by ONR). The present work followed generally the outline of proposals entitled "Storage of Solar Energy Through Valence Photoisomerization," (11/1/75 - 1/31/77), "Quinone Cycloadditions: Photochemistry Using Visible Light" (2/1/77 - 1/31/78), and "Photochemistry Involving Charge Transfer Excited States" (2/1/78 - 2/28/79)

The focus of the research was examination of isomerization and cycloaddition reactions which can be driven by relatively low energy radiation (near ultraviolet and visible light). Most of the reactions studied were thermally reversible thus constituting photochemically driven reaction cycles which potentially store significant quantitites of photon energy. Potential applications for such reactions include photochemical storage of solar energy and photochromism suitable for optical memory devices. The research involved in part a study of the photochemistry of visible absorbing charge transfer complexes. These efforts were expanded to include preliminary investigations of the charge transfer excited states of an important family of laser dyes, the amino substituted coumarins.

ACHIEVEMENTS OF THE PROGRAM

(1) Criteria for the successful storage of photon energy as latent heat through valence photoisomerization have been outlined.[1] Energy storing reactions and potentially useful substrates for photochemical storage have been identified. Economic constraints on the selection and service life of photochemical materials to be used in solar energy storage units have been evaluated.

(2) Several prototype photochemically induced valence isomerizations have been evaluated.[2,3] Quantum efficiencies, storage enthalpies, and recycle capability were determined for these systems.

(3) The mechanisms of several energy storing photoisomerizations were studied.[3-5] For internal cycloadditions (the most useful class of energy storing isomerizations), evidence for the intermediacy of biradicals was obtained. Partitioning of these intermediates was identified as the most important determinant of quantum efficiency for photoisomerization. The study of cycloaddition mechanism for a series of linked anthracenes provided an important evaluation of excimers and biradicals in the well known anthracene photodimerization reaction.

(4) Cycloaddition and other reactions of substrates having visible absorbing chromophores were studied.[6-9] An investigation of biacetyl photoaddition to alkenes (which leads to small ring oxetane cycloadducts) included determination of biacetyl phosphorescence quenching constants and quantum efficiencies, multiplicity, and stereochemistry of addition reactions.[7,8]

(5) Charge transfer complexes of tetracyanoethylene[10] and chloranil[11] with potential alkene photoaddends were characterized. Visible absorption spectra for these complexes were found to be chiefly influenced by the electron donor ability of the alkenes. Photoreactions of chloranil/alkene CT complexes were identified, including photoaddition and chloranil photoreduction.[11]

(6) Investigation of courmarin laser dyes[12] included the determination of solvent effects on the wavelength and yield of coumarin fluorescence emission, and an evaluation of potential quenchers of dye fluorescence and dye triplets.

(7) Energy storing organic photoreactions were reviewed with emphasis on photosensitization mechanisms which allow the use of longer wavelength radiation in driving photoisomerizations.[13] The potential importance of thermal activation

of low energy longlived excited species (the temperature dependence of quantum yields of photoreactions which employ low energy photons) was established.

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WORK IN PROGRESS - FUTURE DEVELOPMENTS

Studies of energy storing photoisomerization reactions are continuing with support from the Department of Energy. For the photoisomerization of a derivative of norbornadiene, the limit of useful wavelengths, for an efficient photoreaction having a large storage enthalpy, has been extended past 500 nm. Studies of the temperature dependent quantum yields of this reaction sensitized by very low triplet photosensitizers suggest that use of visible light to at least 600 nm will be possible. Exciplex (electron transfer) mechanisms as well as energy transfer mechanisms of photosensitization are presently under investigation.

Study of coumarin laser dye photochemistry and photophysics continues with the joint sponsorship of the ONR chemistry and physics programs. The objective of this work is improvement of the efficiency and service life of laser dyes with the determination of factors influencing dye emission yields and the identification of dye photodegradation paths and their mechanisms.

A study of the photochemistry of chloranil/alkene charge-transfer complexes has been completed. Submission of a technical report (No. 10) concerning this work is planned.

PUBLICATIONS AND PRESENTATIONS CITING ONR-ARPA SUPPORT

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(14) "Photosensitization Mechanisms for Energy Storing Isomerizations," G. Jones, II, P.T. Xuan, and S.-H. Chiang, in "Solar Energy: Chemical Conversion and Storage," Ed., R.R. Hautala, R.B. King, and C. Kutal, The Humana Press, Clifton, N.J., 1979

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