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PHOTOSENSITIZATION MECHANISMS FOR ENERGY STORING ISOMERIZATIONS--ETC(U)
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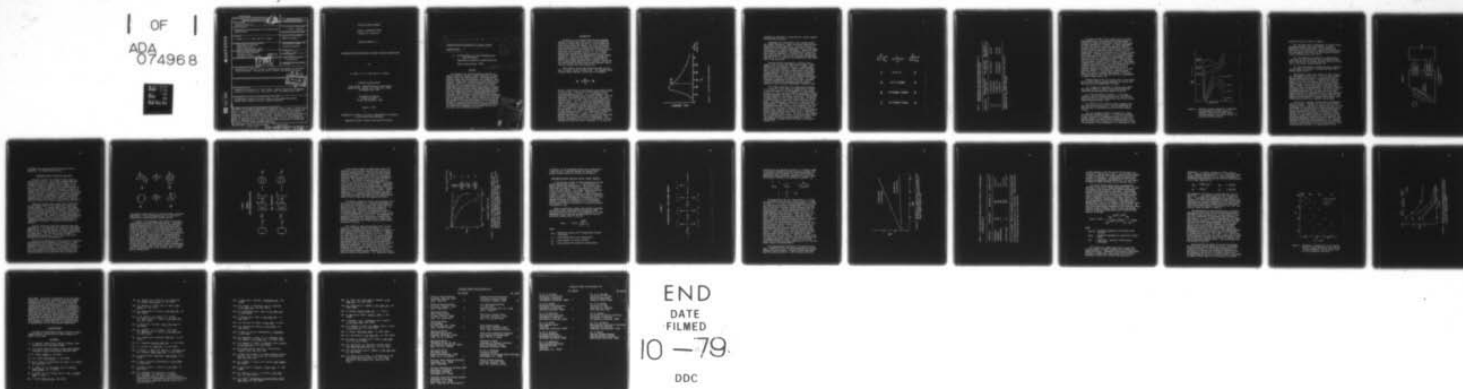
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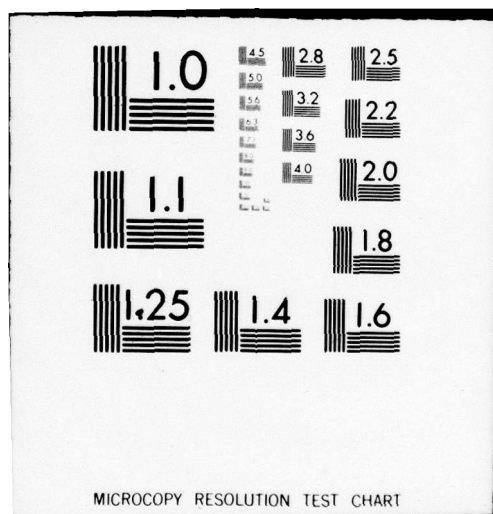
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PHOTOSENSITIZATION MECHANISMS FOR ENERGY STORING ISOMERIZATIONS

BY

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ABSTRACT

The prospects for driving endoergic reactions of simple, relatively abundant, organic chemicals by photochemical means have been examined. Photoisomerization reactions which have some potential for storage of solar energy as latent heat in kinetically stable products are surveyed. Emphasis is placed on methods for the photosensitization of storage chemicals to visible light. Mechanisms include excited state complexation of isomerizable substrates through electron donor-acceptor attraction and conventional energy transfer photosensitization. Efficient isomerization of a norbornadiene derivative using the latter technique and photosensitizers absorbing past 500 nm is described. Factors controlling the efficiency of endothermic triplet energy transfer are outlined. The concept of "thermal upconversion" of the excitation energies of visible absorbing sensitizers is introduced, including a demonstration of improved quantum efficiency as a function of temperature for an isomerization which utilizes a very low energy sensitizer.

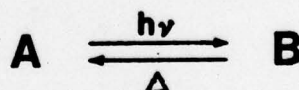
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INTRODUCTION

Interest in solar energy conversion has expanded rapidly in recent years due in part to the recognition that use of solar power represents a sensible match between energy supply and demand. The wide distribution and low energy density of sunlight are especially well suited for a host of applications with low power requirements and little economy of scale (1). It is widely appreciated, nonetheless, that the success of solar devices will depend on the development of energy storage capability. Much research effort is now directed to methods of storage of solar energy as latent heat (2). Use of phase change materials (e.g., eutectic salts) (3) has received most attention and is most advanced; thermochemical methods have been proposed (4).

Photochemical latent heat storage has been the subject of several recent reviews (5-8). The proposed energy storage scheme involves a closed cycle of reactants



which is light driven in one direction and releases energy in the reverse. Selection of A and B depends on the following general criteria. (1) A must absorb or be sensitized to atmospherically filtered sunlight. The most important, high energy portion of the solar insolation spectrum (fig. 1) is 300 - 700 nm, including most of the visible region. (2) To insure that photochemistry proceeds in one direction, B should not absorb solar intensity or be involved in energy transfer with a sensitizer. (3) The quantum efficiency of photoreaction $A \rightarrow B$ must be near unity. (4) Thermal reaction $(B \rightarrow A)$ should have a large negative enthalpy. (5) Photoproduct B should be kinetically stable (i.e., revert to A negligibly at ambient temperatures). Ideally a catalyst can induce back reaction at a controllable rate and temperature. (5) Chemical components must survive a large number of energy storage and reversion cycles. Chemicals, A - B, must be

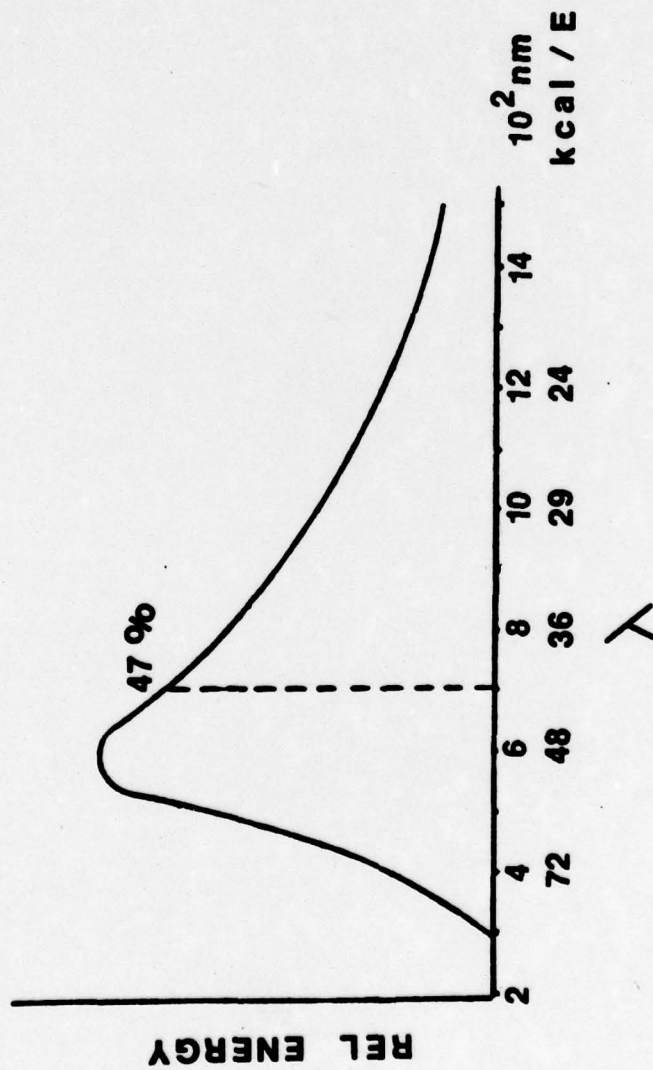


Figure 1. The Solar Insolation Spectrum.

inexpensive, available in large quantity, readily handled and relatively non-toxic.

Advantages of a photochemical heat storage system are readily identified. Many light driven reactions have large energy storage capacities. Storage of energy is possible at low collector temperatures and on cloudy days (efficient use of shorter wavelengths). Compared to other solar-thermal transducers, the photochemical system will have lower requirements for collector size, storage area, and insulation (9). Heat can be retrieved (through back reaction of B) at relatively high temperatures (even above that of the collector).

Selected organic photochemical reactions meet a number of the criteria for latent heat storage. Simple unimolecular rearrangement reactions, or photoisomerizations, are most attractive. Many of these rearrangements, particularly valence isomerizations, have large storage enthalpies and involve relatively low molecular weight materials. A number of the potential photoisomerization substrates are liquids of moderate volatility which can be readily circulated and stored. The simple inexpensive engineering of flat plate solar collectors (1,2) and storage heat exchangers could be readily adapted for use with these photochemical working fluids.

Four isomerization pairs are shown with structures 1 - 8, part of a large family of isomerizations related to the interconversion of norbornadiene (1) and quadricyclane (2). Data for these examples are shown in Table I including quantum efficiencies for the photochemical step, storage enthalpies, and thermal stabilities. The ability of these systems to store impressive amounts of chemical potential energy in relatively "stable" molecules is well known. The thermodynamic instability of quadricyclane photoproducts is understood in terms of bond angle strain introduced when small (three or four membered) rings are formed (15). The kinetic stability of photoisomers is possible (back reaction is slowed) due to a high potential barrier which separates the isomers which is imposed by orbital topology factors (16). The rates of back reaction can be modified using a variety of transition metal catalysts which provide low energy pathways for thermal rearrangement, a general result for small ring organic systems (17).

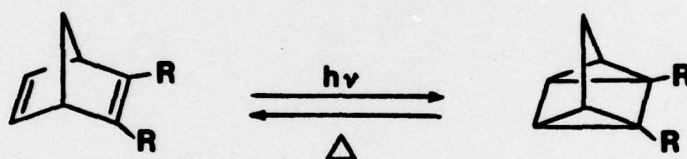
1 $R = H, H$ 23 $R = H, CO_2Me$ 45 $R = CO_2Me, CO_2Me$ 67 $R = CO_2Me, C_6H_5$ 8

Table I. Photochemical and Thermal Reaction Parameters for Norbornadiene-quadracyclane Isomerizations

Isomerization	Quantum efficiency (λ , nm) (ref)	ΔH_{AB} (kcal/mol) (J/g) (ref)	Back Reaction Temperature ($^{\circ}\text{C}$) ^b
1,2	0.7 ^a (313)(10)	26.7(1190)(11)	135-200
3,4	0.9 ^a (313)(12)		
5,6	0.5(300) (13)	18.5(372)(14)	115-180
7,8	0.6(334)(15)	23.0(433)(5)	100-160

^aPhotosensitized. ^bTemperature range for back reaction at moderate rate (half-life = minutes).

As shown in Figure 2 for a hypothetical reversible photoisomerization, the combination of thermodynamic instability (large ΔH) and kinetic stability (large $\Delta H^\ddagger$) presents something of a dilemma. As longer wavelengths of light are used and increasing amounts of chemical potential energy are stored, excited states with reduced driving force are required to mount a barrier in the ground state surface of increasing size, in order to reach photoisomer. Although the severity of this complication is not yet known (vide infra) it seems prudent to project that 700 nm will be a boundary for wavelengths of solar emission useful for photoisomerization, if storage capacity and energy retention are to remain high. The organic isomerization systems provide an interesting contrast with inorganic electron transfer reactions (18) which in principle allow use of longer wavelengths but with severely reduced storage capability (low barrier to back electron transfer). The molecular inorganic system, $\text{NOCl} \rightarrow \text{NO} + \frac{1}{2}\text{Cl}_2$, is another photochemical latent heat storage system for which the back reaction is spontaneous at ambient temperatures (19).

Progress made in the last several years in the assessment of photon energy storage properties of organic isomerizations can be summarized as follows.

(1) A number of reactions or reaction types which have some promise for photon energy storage have been identified and quantitatively studied (5, 20-24).

(2) The norbornadiene system ($1 \rightarrow 2$) has been studied in detail, including extension of the threshold wavelength for efficient isomerization past 400 nm (using organic photosensitizers) (10).

(3) Metal ions or transition metal complexes have been used to drive reaction of 1 and the mechanisms of this new mode of photosensitization have been explored (25,26).

(4) The secondary chemical components of a solar photo-thermal system involving $1 \rightarrow 2$ have been developed. A novel feature of this demonstration unit is the use of polymer supports to anchor organic photosensitizers (10) and transition metal catalysts (for back reaction) (27,28). The deployment of these components in a photochemical solar

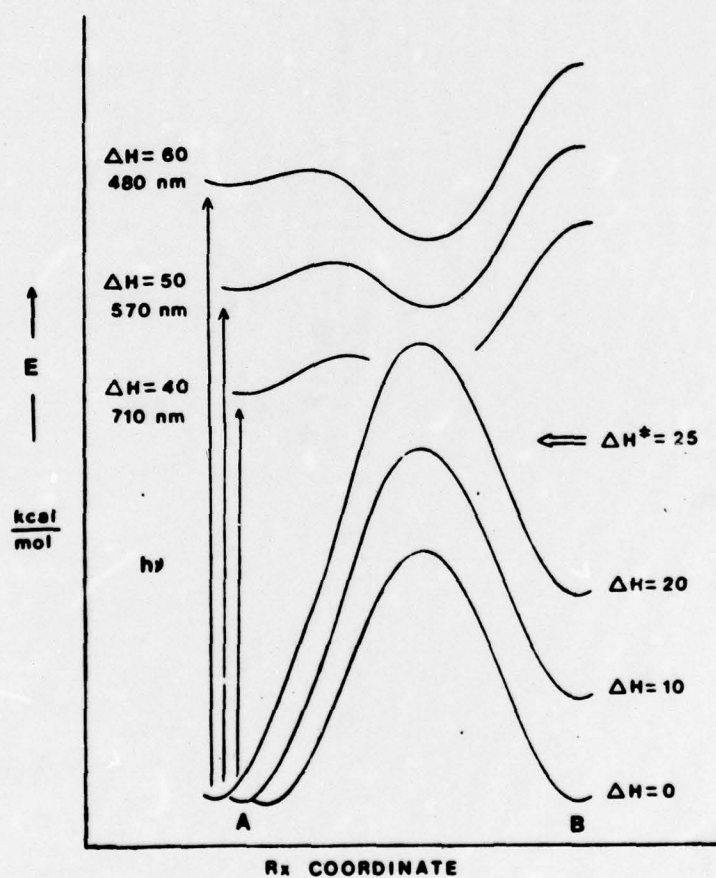


Figure 2. Potential surface diagram for a hypothetical photochemical reaction which is thermally reversible and which stores variable amounts of excitation energy in a kinetically stable product.

conversion device is shown in Scheme 1.

(5) The penultimate intermediates in energy storing photoisomerizations have been proposed in several mechanistic studies (21,29,30). Thus formation and partitioning of biradicals are expected to ultimately control the quantum efficiencies of most potentially useful organic photoreactions (*vide infra*).

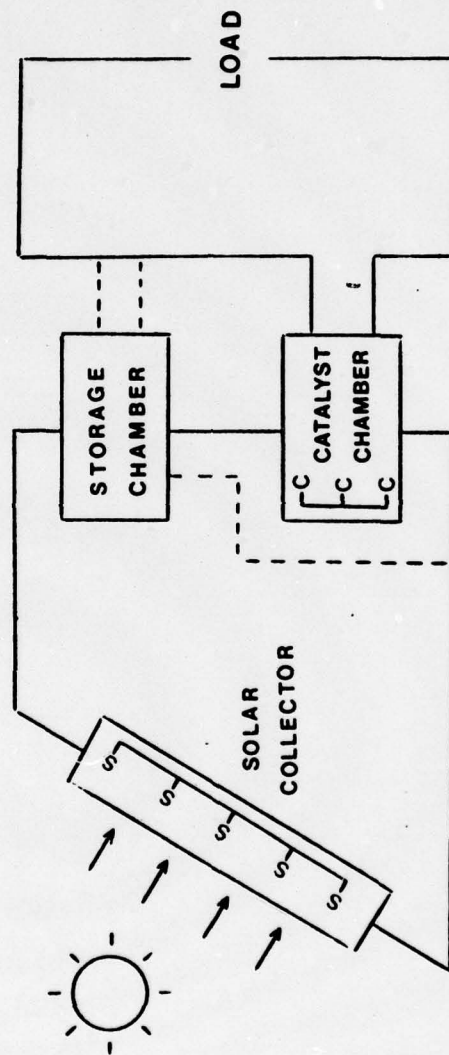
(6) The comparative economics of a photochemical latent heat storage system has been assessed with particular reference to the storage capacity, service life and cost of the primary storage chemical (9).

(7) New developments in photocalorimetry techniques have provided a ready means for measuring latent heat storage capacities (31).

Photochemical latent heat storage of solar energy is far from demonstrated utility. It is important to note what performance features of an eventual solar photo-thermal unit remain in doubt. Practicability does not appear to rest with the storage capacity of (organic) photoreactions or with other intrinsic chemical limitations. Systems with unidirectional, high yield photochemistry, large storage enthalpies, and kinetic stability in photoproducts are readily found. The more illusive performance objectives are the extension of the wavelength threshold for photochemical use of solar radiation, demonstration of the durability of working chemical components, and development of systems within rather strict limitations on the cost of chemicals and hardware.

The following passages include recent photochemical results directed to meeting the first of the following objectives which we consider of highest priority: (1) the development of photosensitization mechanisms which allow use of very low energy photons in driving photoisomerizations (extension of the solar threshold to at least 600 nm); (2) the identification of inexpensive primary chemicals (isomerization substrates) which have the required thermochemical properties and are compatible with developing photosensitization techniques; (3) continued matching or tailoring of photosensitizers and catalysts with the storage medium to insure the efficiency of light harvesting and recycling; (4) demonstration of the

Scheme 1



S = PHOTOSENSITIZER
C = CATALYST

resistance of a system to fatigue (a proper order of magnitude = 100 photo-thermal cycles).

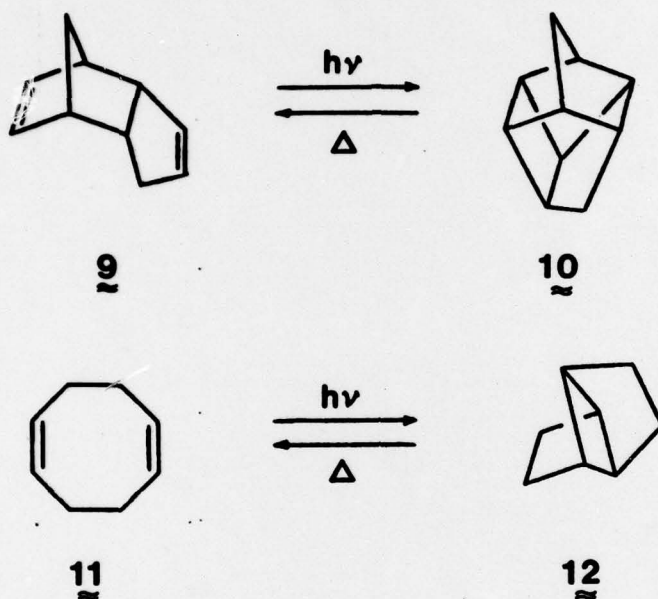
PHOTOSENSITIZATION INVOLVING EXCIPLEXES

The unit of merit for storage of solar energy as latent heat is 10^6 kJ. This figure somewhat more than accounts for the daily heating load in winter for an average dwelling in a moderately cold climate in the U.S. (2). Assuming a capacity for a storage chemical of 100 kJ (about 20 kcal)/mol and 10 mol/kg, a material requirement for reversible storage of 10^6 kJ of 1000 kg is readily calculated. If the cost of a storage raw material is to stay below a recommended (3) \$2,000, (a three-year lifetime for the storage medium, probably 2-300 latent heating cycles), then the cost of the primary chemical should be no more than \$2/kg or something less than \$1/lb.

These cost figures place rather severe limitations on the eventual choice of an economically competitive storage chemical. If storage capacity per unit weight is to remain high and the cost of synthetic modification of basic industrial raw materials held to a minimum, then the choice of chemicals for use on a large scale rests with a relatively small number of abundant photochemically active materials. Since it is not in general possible to incorporate elaborate light harvesting chromophores in isomerization substrates, photosensitization must be employed.

Several inexpensive industrial chemicals have been suggested (6,7) as candidates for relatively large scale photochemical latent heat storage including dicyclopentadiene (9) and 1,5-cyclooctadiene (11) whose isomerizations are shown below. The list may include a number of norbornadienes (especially 1 and 5) whose large scale manufacture should be straightforward.

The classical mechanisms of sensitization in solution photochemistry involve bimolecular encounters of light-capturing agent and reactant leading to either energy transfer or electron transfer. An important rendition of the latter is exciplex formation, the binding of sensitizer and substrate as an electron donor-acceptor pair. Excited complexes, which depend for their existence on

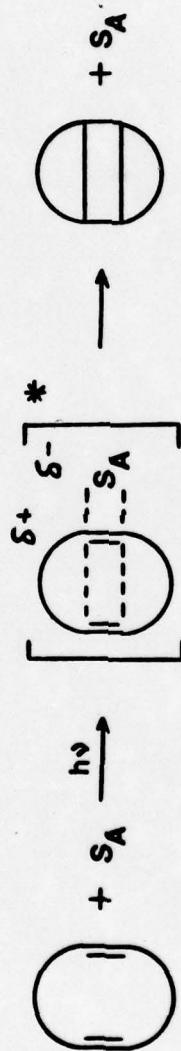


the powerful redox properties of excited states, have been implicated in a host of photoreactions in a variety of spectroscopic and photokinetic studies (32,33).

A number of rearrangements that qualify as exciplex isomerizations have been identified (34-39). Importantly these photoisomerizations are induced by electron donor-acceptor complexation of a light absorbing agent with a substrate for which low lying excited states do not exist or are not deployed. In a recent publication (7) we describe the application of this principle to the activation of a number of photoisomerizable non-conjugated dienes which have energy storage potential. The mechanism proposed for exciplex isomerization is shown in Scheme 2. The induction of isomerization may be viewed as a template effect resulting from electronic polarization by the excited sensitizer. Exciplex decay leading to photoisomer is thought possible since either electron loss or electron gain in the diene portion of the exciplex leads to transannular bonding (40).

Scheme 2

REDOX
PHOTOSENSITIZATION



EDA EXCIPLEX



In our study a number of hydrocarbon dienes with relatively low ionization potentials were paired with aromatic photosensitizers. The electron donor dienes were shown to quench the fluorescence of the electron acceptor aromatics at variable rates which depended on sensitizer and substrate ability to accept and donate electrons. The falloff of quenching rate shown in Figure 3 is consistent with the thermodynamics of electron transfer in an encounter complex (41). Independent evidence that exciplexes are formed between dienes and sensitizers came from the observation of weak, long wavelength exciplex emission in non-polar solvents. Unfortunately, in this series exciplex decay did not lead to photoisomers. A competing reaction between photosensitizers and substrates (cycloaddition) was identified and shown to have a relatively high quantum efficiency.

The opposite regime of electron donor-acceptor interaction was also examined (7). Acceptor norbornadiene 5 was paired with fluorescent donor sensitizers which displayed a range of redox and absorption properties. In this series, two sensitizers were found effective. Irradiation (290 - 340 nm) of 2-methoxynaphthalene or 2,6-dimethoxynaphthalene in the presence of 5 gave 6 with a limiting quantum efficiency of 0.3. The dependence of quantum yield on quencher concentration revealed that naphthalene singlets were responsible for isomerization. Emission-reabsorption and Forster energy transfer mechanisms were ruled out.

This example of redox sensitization (42) via exciplexes for an energy storing isomerization ($5 \rightarrow 6$) is potentially extendable and may be related to the metal or metal complex sensitization mechanism (25,26). However, the improvement in spectral sensitivity of 5 in combination with the donor naphthalenes is not significant and the redox sensitizers which absorb at longer wavelengths led to unproductive exciplex decay. We are encouraged nevertheless that all desirable substrates appeared to form excited complexes with sensitizers having a range of absorption properties. Two features of the exciplex mechanism for diene isomerization should be kept in mind in designing new systems. (1) Reactive positions in sensitizer may promote exciplex cycloaddition at the expense of exciplex isomerization. (2) Appreciable overlap

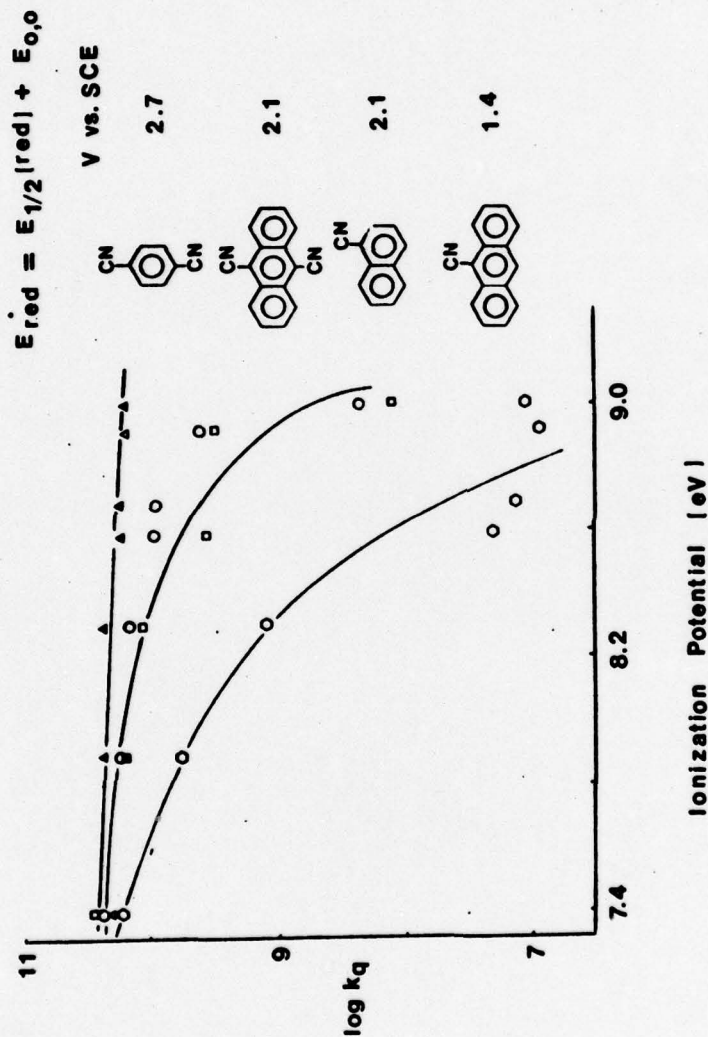


Figure 3. Stern-Volmer constants for the quenching of aromatic nitrile fluorescence in acetonitrile as a function of ionization potential of non-conjugated dienes (including 2, IP = 7.4 eV). Nitriles are shown opposite appropriate curves along with excited state reduction potentials (V vs. SCE).

of orbitals in non-conjugated dienes (more pronounced in 5 than in 9 or 11) may be required for nascent trans-annular bonding within the lifetime of exciplexes.

PHOTOSENSITIZATION INVOLVING TRIPLET ENERGY TRANSFER

In the earliest studies of photoisomerization of the parent norbornadiene system, $1 \rightarrow 2$, sensitization via energy transfer was employed (43). The classical mechanism shown in Scheme 3 involves excitation of a sensitizer (S) which absorbs in a useful region and produces triplet excited states in high yield. Sensitizer triplets, if sufficiently energetic, transfer excitation energy to quencher molecules (Q) which lead to product (P) usually by way of a photochemical intermediate (I). The quantum efficiency for formation of a triplet derived product is substantially improved if Q is a relatively poor absorber and/or if the yield of Q triplets on direct irradiation is low.

Using a conventional steady state kinetics technique and making several relatively safe assumptions about processes which are not likely to be competitive for room temperature fluid solutions, an expression for the isomerization quantum yield is derived.

$$\phi_{\text{isom}} = \phi_{\text{isc}} P_i \frac{k_q[Q]}{k_q[Q] + k_d}$$

where

ϕ_{isc} = sensitizer triplet yield (intersystem crossing efficiency)

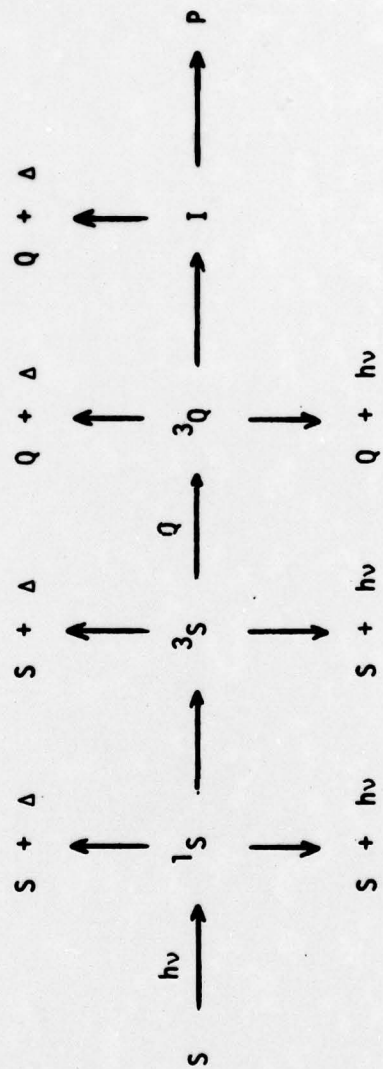
P_i = partitioning factor for intermediate I

k_q = rate constant for energy transfer

k_d = rate constant for sensitizer triplet decay

Scheme 3

PHOTOSENSITIZATION - TRIPLET ENERGY TRANSFER



Inversion of this expression results in a function linear in reciprocal quantum yield and reciprocal quencher concentration, with an intercept to slope ratio relating bimolecular and unimolecular components of triplet decay (and triplet lifetime in the absence of quencher, τ_0).

$$\frac{1}{\phi_{\text{isom}}} = \frac{1}{P_i \phi_{\text{isc}}} + \frac{k_d}{P_i \phi_{\text{isc}} k_q [Q]}$$

$$\frac{i}{s} = \frac{k_q}{k_d} = k_q \tau_0$$

A concentration plot for isomerization $5 \rightarrow 6$ using two sensitizers with different triplet energies is shown in Figure 4. The almost negligible dependence on $[5]$ for the high energy sensitizer, benzophenone, is consistent with a high rate of energy transfer quenching (near the diffusion limit). The more pronounced sensitivity for camphorquinone sensitized isomerization reflects a reduced quenching rate constant, no doubt the result of a lower sensitizer triplet energy. Other data shown in Table 3 confirm the dependence on sensitizer triplet level. Sensitizers with excitation energies 53 kcal/mol and greater are sufficiently energetic to drive the reaction at low concentrations of quencher whereas less robust excited triplets require high concentrations of 5 for efficient reaction. It is important to note that camphorquinone and acridine orange are effective sensitizers for isomerization of 5 at high substrate concentration. The absorption of these sensitizers just past 500 nm extends significantly the threshold of photoactivity well into the visible. With this system, 17% of the total solar energy spectrum is absorbed and about 20% of absorbed energy is stored. Indeed the low energy sensitizers bring about rapid conversion of 5 to 6 in sunlight in small scale experiments.

The norbornadienes constitute an interesting structure - reactivity series for photoisomerization utilizing photons of minimal energy. Previous studies have shown that efficient reaction of 1 and 3 requires sensitizer

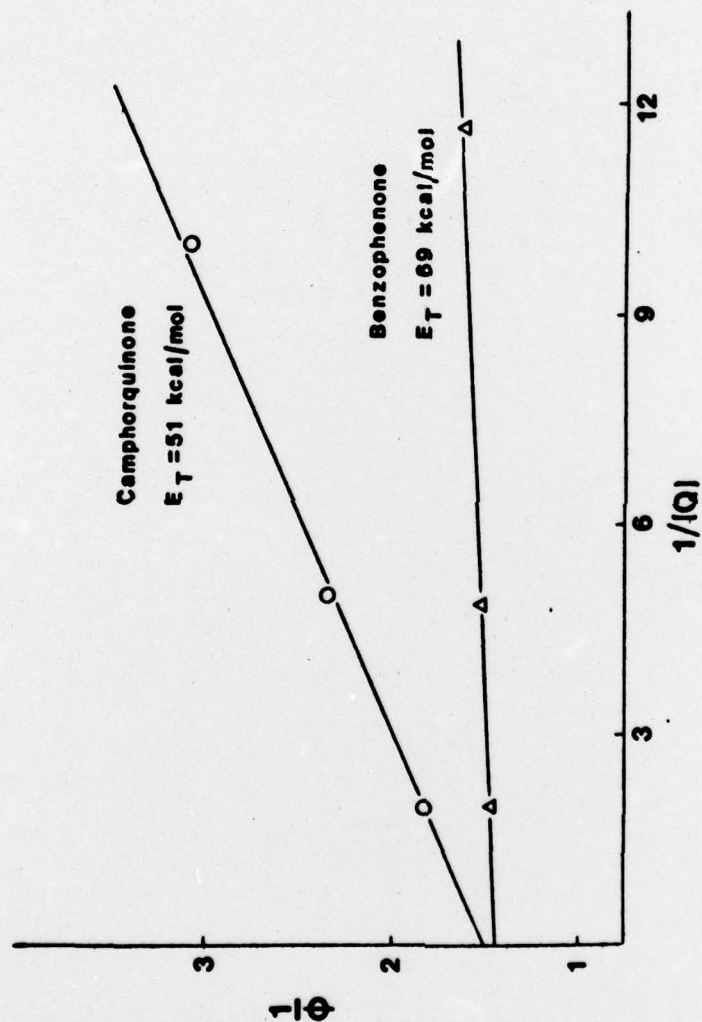


Figure 4. Dependence of isomerization ($\delta + \epsilon$) quantum yield on the concentration of s (photosensitizers as shown, benzene solvent, 30°).

Table 3. Triplet Sensitized Isomerization of Dimethyl 2,3-norbornadiene-dicarboxylate (5)

Sensitizer	E_T (kcal/mol)	Wavelength, nm	Quantum Yield ^{a,b}
benzophenone	68	366	0.6 (0.7)
fluorenone	53	366	0.6
camphorquinone	51	435	0.3
		480	0.3 (0.6)
acridine orange	49	366	0.01 (0.2) ^c

^a0.1 M 5 in benzene. ^bValues in parenthesis are limiting quantum yields calculated by extrapolation ($1/\phi$ vs. $1/[5]$ plots). ^cValues diminished by low intersystem crossing yield (0.4) of sensitizer.

triplet energies of 65 (10) and 58 (12) kcal/mol, respectively. From the data above, a minimum triplet energy of about 50 kcal/mol for isomerization of diester derivative 5 is indicated. Corresponding minimum singlet energies and absorption thresholds for 1, 3, and 5 would be about 70 (400), 63 (450), and 55 kcal/mol (520 nm).

Are these triplet energy minima insurmountable barriers to the use of longer wavelength light? We think not based on our analysis of the important parameters controlling energy transfer efficiency. Where energy transfer from sensitizer triplets to substrate is endoergic, the quantum yield of sensitized isomerization is sharply dependent not only on sensitizer triplet lifetime and quencher concentration as shown above but also on the temperature of the medium. Large temperature dependences of the rate of endoergic triplet energy transfer have been observed for several systems (44-45). We have used relationships developed in the pioneering energy transfer study of Sandros (44) to express the quantum yield of sensitized isomerization as a function of temperature as follows.

$$\phi_{\text{isom}} = \phi_{\text{isc}} P_i \frac{A_{\text{dfe}} e^{-E_{\text{df}}/RT} e^{-\Delta E_{\text{T}}/RT} [Q]}{A_{\text{dfe}} e^{-E_{\text{df}}/RT} e^{-\Delta E_{\text{T}}/RT} [Q] + A_{\text{de}} e^{-E_{\text{d}}/RT}}$$

where

$A_{\text{df}} \cdot E_{\text{df}}$ = Arrhenius parameters for diffusion rate constant

$A_{\text{d}} \cdot E_{\text{d}}$ = Arrhenius parameters for sensitizer triplet decay

ΔE_{T} = Sensitizer - quencher triplet energy difference

The results of a model study clearly reveal the salutary effect of higher temperatures on photoisomerization efficiency. Parameters were chosen as shown below defining a system with a rate constant for diffusive encounter of sensitizer triplets and substrate of

$10^{10}\text{M}^{-1}\text{sec}^{-1}$, a triplet lifetime of 10^{-5}sec (both at 25°), a quencher concentration of 1 M, a sensitizer intersystem crossing efficiency of 1.0, and an intermediate (biradical) partitioning constant (limiting quantum yield) of 0.7 (that found for δ).

$$A_{df} = 10^{12}\text{M}^{-1}\text{sec}^{-1} \quad E_{df} = 3 \text{ kcal/mol}$$

$$A_d = 10^7\text{sec}^{-1} \quad E_d = 3 \text{ kcal/mol}$$

The parameters are similar to those found for rates of diffusion and triplet decay (47) for relevant systems. The temperature independence of ϕ_{isc} and P_i is assumed, the latter substantiated by recent findings (29) concerning the internal cycloaddition of an enone triplet. Calculated isomerization quantum yields for three sensitizer triplet deficiencies (7-9 kcal/mol) for a 150° temperature range are shown in Figure 5.

The enhancements in quantum efficiency at elevated temperatures (up to $25X$) for sensitized isomerization of the model system are impressive. We have sought to confirm this improvement in performance with reference to the system $\delta \rightarrow \epsilon$. A sensitizer, benzanthrone, was chosen whose triplet energy ($E_T = 46 \text{ kcal/mol}$ from emission (48) and energy transfer (49) measurements) falls well below that of δ ($E_T \sim 53 \text{ kcal/mol}$ according to the camphor-quinone and acridine orange sensitization results). Quantum yield data for four concentrations and three temperatures are shown in Figure 6. The combined effects of temperature and concentration amount to enhancement of quantum efficiency of $\sim 50X$ ($.005 \rightarrow .21$). We are presently extending the study to higher temperatures in order to show that this reaction which stores an enormous fraction of excitation energy ($19/46 = .42$) can proceed with high quantum efficiency.

The possibility of making up excited state energy deficiency with thermal energy (as much as 10 kcal/mol) is most attractive. If the "thermal upconversion" of triplets is translated into absorption thresholds (singlet energies), the use of, for example, 610 nm light (47 kcal/Einstein) to drive a reaction normally considered to require 510 nm light (57 kcal/Einstein) is readily

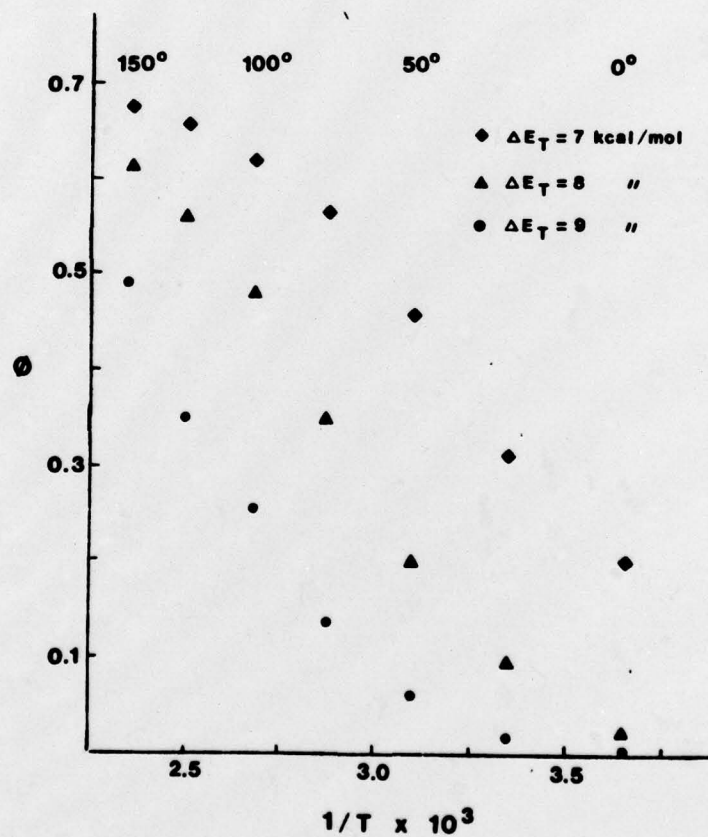


Figure 5. Dependence on temperature of the quantum yield of a model photosensitized reaction involving endoergic triplet energy transfer (for parameters, see text).

envisioned. This shift in wavelength to the red corresponds to an increase in fraction of total solar energy absorbed from 17 to 33% (50). The potential benefits in exploiting the elevated temperatures of solar collectors by using solar energy which is not absorbed by photochemical components but which heats the photoactive medium are largely unexplored. The sensitized organic isomerizations will provide an important test of performance and solar spectral response due to a fortunate coincidence of properties which include the suitability of long lived dye triplets for photosensitization, the desirability of high concentrations of substrate (for high volumetric storage capacity), and the persistence of photoproducts at well above ambient temperatures.

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