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ORGANIC PHOTOCHEMICAL STORAGE OF SOLAR ENERGY

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ABSTRACT

Photosensitization mechanisms for driving energy storing reactions of readily available organic compounds have been studied. Aromatic sensitizers were used as complexing agents for a series of non-conjugated dienes which are capable of valence isomerization. Diene exciplexes, shown to be stabilized by electron donor-acceptor interaction, led to photoisomers with high chemical and quantum efficiency in two of the cases studied. For other systems, sensitizer-diene photoaddition reactions were observed.

Exciplex isomerization of quadricyclanes and hexamethyldewarbenzene was studied. Factors determining the efficiency of rearrangement of excited complexes were examined including the role of exciplex excitation energy in controlling the novel adiabatic exciplex isomerization of hexamethyldewarbenzene.

With triplet photosensitizers visible light (to 520 nm) was used to bring about an energy storing valence isomerization of a diester derivative of norbornadiene. High quantum yields (0.6) were measured at the longest wavelengths yet utilized for this type of isomerization. The quantum efficiency for isomerization using a very low energy triplet sensitizer was significantly enhanced at slightly elevated temperatures, suggesting that thermal energy (in amounts present in solar collector media) can be an aid in driving energy storing photo-reactions.

ORGANIC PHOTOCHEMICAL STORAGE OF SOLAR ENERGY

INTRODUCTION

The study of mechanisms by which energy storing organic photoreactions are driven with relatively low energy (potentially solar) radiation continues. The valence isomerization of simple, readily available non-conjugated dienes such as **1**, **3**, and **5** is of particular interest. Compounds of this sort have conventional photoreactivity (formation of **2**, **4a**, and **6**)¹ only at short wavelengths (< 300 nm). We have examined new methods of photosensitization for these reactions employing systems which involve the two principle categories of interaction between light harvesting agent and isomerizable substrate, electron transfer and energy transfer. The matching of electron donors and acceptors is expected to lead to photoproducts by a mechanism involving exciplexes as shown in Scheme 1. Under the energy transfer theme, factors governing the efficiency of photosensitization (e.g., temperature dependence) for very low excitation energy, visible absorbing triplet photosensitizers are of interest.

RESULTS AND DISCUSSION

Electron Donor-acceptor Exciplex Isomerization. A number of hydrocarbon dienes (e.g., **1**, **3**, and **5**) having relatively low ionization potentials were paired with a series of aromatic photosensitizers. The latter were chosen for their strong electron affinities and their varied absorption in the region 300 - 450 nm. 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 1 is consistent with the thermodynamics of electron transfer in an encounter complex.² Independent evidence that exciplexes are formed between the isomerizable substrates and the acceptor sensitizer

1

2

3

4

5

6

REDOX PHOTOSENSITIZATION

EDA EXCIPLEX

Figure 1 Stern-Volmer constants for the quenching of aromatic nitriles vs. ionization potentials of diene quenchers. (Sensitizers with E_{red}^* values as follows, Δ 1,4-dicyanobenzene, 2.7 V, $\circ$ 1,4-dicyanoanthracene, 2.1 V, $\square$ 1-cyanonaphthalene, 2.1 V, $\diamond$ 9-cyanoanthracene, 1.4 V vs. SCE). Data for quadricyclene (2) (IP = 7.4 eV) are included.

aromatics came from the observation of weak, long wavelength exciplex emission in non-polar solvents.

Photoisomerization products (e.g., **2**, **4**, and **6**) were obtained using reported procedures and sensitive gas chromatographic methods for their assay were established. For the larger group of donor dienes, under conditions of light absorption by the acceptor sensitizers and fluorescence quenching (exciplex formation), photoisomerization was not observed. A competing photoreaction between photosensitizer and dienes (cycloaddition) was identified and shown to have a significant quantum efficiency. Typical cycloaddition results are shown in Figure 2 where 1-cyanonaphthalene is the photosensitizer. The concentration profile is consistent with the involvement of aromatic sensitizer singlets (and exciplexes) in fluorescence quenching (i.e., that the chemical result of singlet exciplex decay is addition to the diene). Quantum yield data for other sensitizer-diene additions which proceed in lieu of isomerization are shown in Table 1.

In contrast to the sensitizer photoaddition results, a bona fide exciplex isomerization of diene **5**, giving **6** cleanly and in good yield, was observed. The aromatic photosensitizers employed so far and their limiting isomerization quantum yields are: 1-cyanonaphthalene (1.0) and 9,10-dicyanoanthracene (0.1). Concentration dependencies showed that the isomerization mechanism involves singlet sensitization. The position of **5** in the fluorescence quenching profile further confirms that an electron donor-acceptor exciplex is involved.

A "reverse polarity" exciplex isomerization was also observed. Norbornadiene derivative **10**, an isomerizable substrate with relatively high electron affinity was paired with electron rich aromatic photosensitizers. With two of these sensitizers, 1-methoxynaphthalene, and 2,6-dimethoxynaphthalene, fluorescence quenching was accompanied by isomerization (**10** $\rightarrow$ **2**). Limiting efficiencies

Figure 2 The dependence of 1-cyanonaphthalene disappearance quantum yield on the concentration of **3** (cyclohexane solvent, intercept, $1/\phi_{lim} = 1.7$)

Table 1. Limiting Quantum Efficiencies for Exciplex Cycloaddition of Electron-acceptor Aromatic Photosensitizers and Non-conjugated Dienes.

Dienes	Sensitizer	ϕ_{lim}^a
1-cyanonaphthalene	0.51
1-cyanonaphthalene	0.88
norbornadiene	1-cyanonaphthalene	0.47
	9,10-dicyanoanthracene	0.06
limonene	1-cyanonaphthalene	0.54
	9,10-dicyanoanthracene	0.02
vinylnorbornene	1-cyanonaphthalene	0.55

^aExtrapolated quantum efficiencies from plots of $1/\theta$ vs. reciprocal concentration of diene in cyclohexane solution (25°).

were 0.3 as shown in the concentration profile (Figure 3).

A portion of these results concerning the exciplex cycloaddition and exciplex isomerization of dienes has been reported.³

Encouraged that properly selected energy storing photoreactions can be generally driven via donor-acceptor exciplexes, we examined two model systems which had been previously reported in order to establish relationships between structure and isomerization reactivity. The conversion of quadricyclene to in the presence of acceptor sensitizers is the oldest example of exciplex isomerization.⁴ In our study, the effect on isomerization yield of substituents on (through examination of and) and the dependence on the nature of the photosensitizer, were for the first time deduced.

Quenching of the fluorescence of several cyano-substituted aromatics by was generally observed. Norbornadiene and cage compound were not

7

R = H

8

9

R = CO₂Me

10

11

12

13

14

Figure 3. The dependence of isomerization quantum yield on the concentration of NOR .

efficient quenchers of aromatic fluorescence. The observed dependence of quenching rate on substrate and sensitizer electron donor and acceptor ability is included in Figure 1. Several photochemical reactions were shown to result from the quenching of aromatic fluorescence. Under conditions where only the fluorophore absorbed light (either 290 - 330 or 330 - 380 nm) exciplex isomerizations $7 \rightarrow 8$ and $9 \rightarrow 10$ were observed. Quenching with norbornadiene (8) led to sensitizer decomposition (cycloaddition of 8 and sensitizers is implicated⁵) but isomerization ($8 \rightarrow 7$) was not observed. Homoquadricyclene (11) did not give 12 in a sensitized reaction but the reverse isomerization ($12 \rightarrow 11$) occurred with low efficiency.

The fluorescence quenching and reaction quantum yield results are shown in Table 2. The data include Stern-Volmer quenching slopes ($k_q\tau$), intercept/slope ratios for plots of $1/(\text{reaction quantum yield})$ vs. $1/(\text{quencher concentration})$, and extrapolated reaction quantum yields (ϕ_{lim}).

The insensitivity of quantum yield for isomerization $7 \rightarrow 8$ to sensitizer structure is significant. Exciplex binding of substrate and sensitizer appear not to control reaction efficiency (compare $k_q\tau$ and ϕ_{lim}). This independence is also apparent in the sensitization of 7 vs. 9 by cyanonaphthalene (i.e., the poorer quencher 9 has essentially the same inherent isomerization efficiency).

In a second model system we showed that the quenching of fluorophores is accompanied by molecular rearrangement ($13 \rightarrow 14$). Quantum yields displayed a concentration dependence consistent with singlet sensitization (Figure 4) (extrapolated quantum yield was near 1.0). Most unusual were the findings concerning exciplex emission which was observed on quenching 1-cyanonaphthalene (CN) and 1,4-dicyanobenzene (DCB). The new emission for these sensitizers paired with 13 was identical to the exciplex fluorescence obtained on quenching the same sensitizers with hexamethylbenzene (14) (λ_{max} 373nm-CN; λ_{max} 392nm-DCB).

Table 2. Fluorescence Quenching and Quantum Yield Data for Sensitization of 7 - 13 by Cyanoaromatics^a

Quencher	Sensitizer	$k_q \tau$	i/s	ϕ_{lim}	Rx observed
7	1-cyanonaphthalene	121.8	73.5	0.74	7 → 8
	anthracene	4.82	4.74	0.65	7 → 8
	9-cyanoanthracene	92.6	81.6	0.31	7 → 8 ^b
	9,10-dicyanoanthracene	151.3	90.1	0.42	7 → 8 ^b
8	1-cyanonaphthalene	23.3	27.6	0.47	sens. decomp
	9,10-dicyanoanthracene	0.21	2.40	0.07	sens. decomp
9	1-cyanonaphthalene	41.8		0.60	9 → 10
12	1,4-dicyanobenzene	56.7	96.1	0.02	12 → 11
13	1-cyanonaphthalene	121.5	204.9	1.01	13 → 14

^aCyclohexane or hexane solvent; [sens.] = 10^{-3} - 10^{-4} M

^bSome sens. disappearance also observed ($\phi = 0.03$)

Figure 4 The dependence of the quantum yield of isomerization on the concentration of HMDB (cyclohexane solvent, 350 nm).

Monitoring of λ_{em} showed that trivial reabsorption-quenching is not responsible for the coincidence of spectra.

In a three component experiment in which 2,4-dimethyl-2,5-hexadiene (DMH) (a second electron donor) was used to quench exciplex emission, Stern-Volmer analysis revealed similar lifetimes for HMB and HMDB derived exciplex emission. Most importantly, CN- λ_{em} exciplex fluorescence could be quenched by DMH at concentrations where sensitized isomerization ($\lambda_{\text{em}}^3 + \lambda_{\text{em}}^4$) was undiminished, showing that the emitting state could not be the source of rearrangement.

Our results are similar to those of Taylor⁶ who examined the CN- λ_{em}^3 pair in non-polar solvents and concluded that exciplex isomerization is adiabatic (i.e., that exciplex emission is a photoproduct-HMB exciplex-fluorescence). The mechanisms (shown simply in Scheme 2) involves the partnership of exciplex donor and acceptor which persists during molecular rearrangement on an excited surface! The results differ considerably from those reported by Evans⁷ concerning exciplex isomerization of λ_{em}^3 in a polar solvent (methanol). In this study exciplex emission was not observed and other evidence (limiting quantum yields $\gg 1$) pointed to a light induced chain mechanism for decomposition of λ_{em}^3 involving radical-ions.

Relative yields of emission derived from λ_{em}^3 and λ_{em}^4 and three acceptor sensitizers were determined. Data points at identical levels of sensitizer quenching gave relative yields for the adiabatic path (the portion of exciplex isomerization which "stores" energy!). Values ranged from 20 - 50% and appeared to depend more on the energy of the λ_{em}^4 exciplex (the adiabatic product) (determined from emission wavelength) than on $E(\text{red})^*$ for the sensitizer (the redox driving force - exciplex binding).

Scheme 2

Photosensitization involving triplet energy transfer. The isomerization $10 \rightarrow 9$ has a large capacity for storing photon energy as latent heat (storage enthalpy = 19 kcal/mol^B). This system has been studied using sensitizers which absorb in the 700 - 500 nm range. The strategy does not combine electron donors and acceptors as described in the previous section but employs photosensitizers which transfer triplet excitation energy according to the mechanism shown in Scheme 3. S, Q, I, and P are respectively the sensitizer, quencher (capable of isomerization), a postulated photochemical intermediate, and photoproduct.

Using a conventional steady state kinetics techniques 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. Inversion of this expression results in a

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

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

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).

Isomerization of 10 was carried out using a number of sensitizers all leading to photoisomer 9 in quantitative chemical yield. Concentration dependencies of isomerization quantum yield were consistent with the relationships shown above, supporting a triplet sensitization mechanism. As shown

Scheme 3

PHOTOSENSITIZATION - TRIPLET ENERGY TRANSFER

in Table 3, sensitizers with excitation energies 53 kcal/mol and greater are sufficiently energetic to drive the reaction at low concentrations of quencher with high quantum efficiency whereas less robust excited triplets require high concentrations of λQ for efficient reaction. It is important to note that camphorquinone and acridine orange are effective sensitizers for isomerization of λQ 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 is stored. Indeed the low energy sensitizers bring about rapid conversion of λQ to Q in sunlight in small scale experiments.

We have found that quantum yields of isomerization upon sensitization by very low energy triplets are not dependent on the concentration of the quencher alone. A relatively large and potentially useful temperature dependence has been observed. We have used relationships developed in the pioneering energy transfer study of Sandros⁹ to express the quantum yield of sensitized isomerization as a function of temperature as follows.

$$\phi_{\text{isom}} = \phi_{\text{isc}} P_i \frac{A_{df} e^{-E_{df}/RT} e^{-\Delta E_T/RT} [Q]}{A_{df} e^{-E_{df}/RT} e^{-\Delta E_T/RT} [Q] + A_d e^{-E_d/RT}}$$

where

A_{df}, E_{df} = Arrhenius parameters for diffusion rate
constant

A_d, E_d = Arrhenius parameters for sensitizer triplet
decay

E_T = Sensitizer - quencher triplet energy
difference

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

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 I_0 in benzene. ^bValues in parenthesis are limiting quantum yields calculated by extrapolation ($1/\phi$ vs. $1/[I_0]$ plots). ^cValues diminished by low intersystem crossing yield (0.4) of sensitizer.

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 I_0). The parameters

$$\begin{array}{ll}
 A_{df} = 10^{12} \text{ M}^{-1} \text{ sec}^{-1} & E_{df} = 3 \text{ kcal/mol} \\
 A_d = 10^7 \text{ sec}^{-1} & E_{df} = 3 \text{ kcal/mol}
 \end{array}$$

are similar to those found for rates of diffusion and triplet decay for relevant systems. The temperature independence of ϕ_{isc} and P_i is also assumed. Calculated isomerization quantum yields for three sensitizer triplet deficiencies (7-9 kcal/mol) for 150° temperature range are shown in Figure 5.

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

Figure 6. Quantum yields for photosensitized isomerization, $5 \rightarrow 6$, as a function of temperature and concentration of **5** (benzene solvent).

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 $1Q \rightarrow 9$. A sensitizer, benzanthrone, was chosen whose triplet energy ($E_T = 46$ kcal/mol from emission and energy transfer measurements) falls well below that of $1Q$ ($E_T \sim 53$ kcal/mol according to the camphorquinone 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).

SUMMARY AND CONCLUSIONS

The quenching of fluorescence of aromatic hydrocarbon photosensitizers by non-conjugated dienes which are capable of undergoing energy storing isomerization has been studied. Evidence was obtained for the formation of diene-sensitizer exciplexes which are stabilized by electron donor-acceptor interaction. These excited complexes in non polar solvents do not lead to ion formation but give cycloaddition photoproducts. In several cases addition of dienes to the sensitizers was observed. In two important cases valence isomerization of the complexed diene resulted from exciplex formation (one with unit quantum efficiency). Studies of model exciplex isomerization systems led to the conclusion that the efficiency of photoreaction depends less on the degree of exciplex binding and more on the structural features which control late stages of isomerization (partitioning of intermediates, etc.). The novel adiabatic exciplex isomerization of hexamethyldewarbenzene was studied in detail; for this reaction a unique determination was made of the fraction of excited complexes which remain on an excited surface while undergoing molecular rearrangement.

A diester derivative of norbornadiene was isomerized with high quantum efficiency to an energy rich photoisomer using visible light (400 - 500 nm).

Several sensitizers capable of transferring triplet excitation energy were successful in driving the reaction with high quantum yields (0.3 - 0.6). A model study showed that quantum efficiencies for sensitized isomerization using very low energy triplets will be strongly temperature dependent. This "thermal upconversion" of excitation energy was demonstrated for one low energy sensitizer and the norbornadiene derivative showing significant enhancements of quantum yields (2 - 10X) for modest temperature increases (5° - 65°).

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