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ORGANIC PHOTOCHEMICAL STORAGE OF SOLAR ENERGY

Progress Report

for the period, February 1, 1979 - January 31, 1980

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ABSTRACT

Study of valence isomerization of organic compounds has focused on two mechanisms of photosensitization involving either electron donor-acceptor interaction or energy transfer. The quenching of fluorescent sensitizers by isomerizable substrates results in the formation of excited complexes. These sensitizer-substrate pairs are highly polarized, leading to changes in bond order for the substrates. For several substrates such as quadricyclene, hexamethyldewarbenzene, and a nonbornadiene derivative, this perturbation results in efficient valence isomerization. Isomerization observed on irradiation of charge transfer complexes of isomerizable substrates is consistent with a similar exciplex - template mechanism.

The energy transfer mechanism of photosensitization has been studied by measuring the temperature dependence of quantum yield for isomerization of dimethyl nonbornadiene-2,3-dicarboxylate sensitized by benzanthrone. From temperature and quencher concentration profiles quenching constants have been obtained which are consistent with an endoergic triplet energy transfer mechanism. The "thermal upconversion" of the low energy triplet of benzanthrone results in a threefold increase in isomerization quantum yield over a 90° temperature range.

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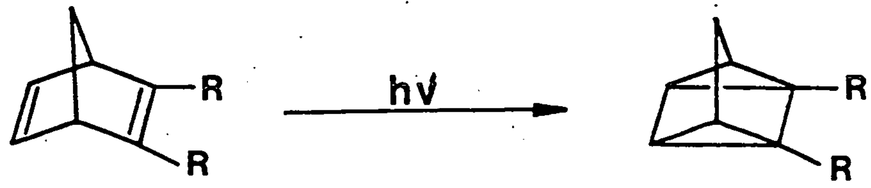
INTRODUCTION

The study of photosensitized valence isomerization of organic compounds has continued. Photosensitizers of the electron and energy transfer type have been utilized in driving isomerization reactions which fall into the categories of internal cycloaddition (e.g., 1 → 2) or cycloreversion (e.g, 2 → 1 or 7 → 8). Important developments for the past year include the following elements. (1) A series of investigations has been completed involving isomerizations which proceed in non-polar solvents via excited complexes (exciplexes) of electron transfer photosensitizers and isomerizable substrates. Important properties of sensitizers and substrates which control the efficiency of isomerization via an exciplex-template mechanism have been identified. (2) Early results concerning the temperature dependence of triplet sensitized isomerization have been extended. Significant increases in quantum efficiency for a system driven by endoergic energy transfer from a low energy sensitizer have been observed. (3) The photochemistry of several charge transfer (CT) complexes has been investigated including the finding that valence isomerization can be driven by irradiation of CT bands.

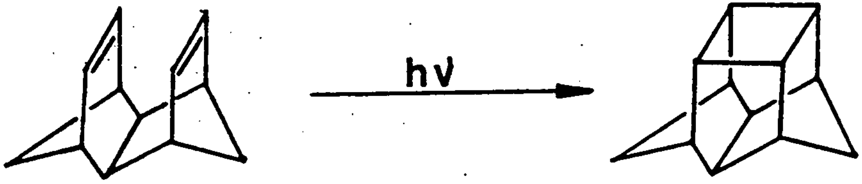
RESULTS AND DISCUSSION

Exciplex systems. A series of non-conjugated dienes and small ring compounds capable of isomerization by internal cycloaddition or cycloreversion have been studied as quenchers of fluorescent sensitizers. In a number of cases fluorescence quenching results in photosensitized reaction. For example, on quenching electron acceptors, 2, 4, 5, and 7 are converted with high efficiency to their respective valence isomers. Similarly the reaction, 3 → 4, is induced on quenching electron donor aromatic fluorophores. Quantum

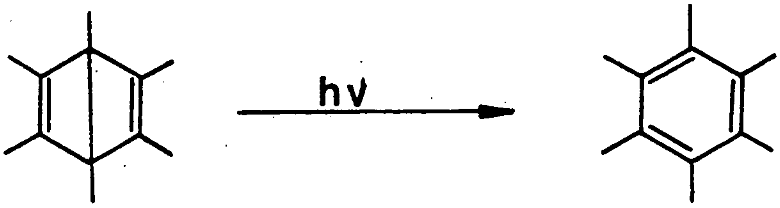


1 $R=H$ 2

3 $R=CO_2Me$ 4



5 6



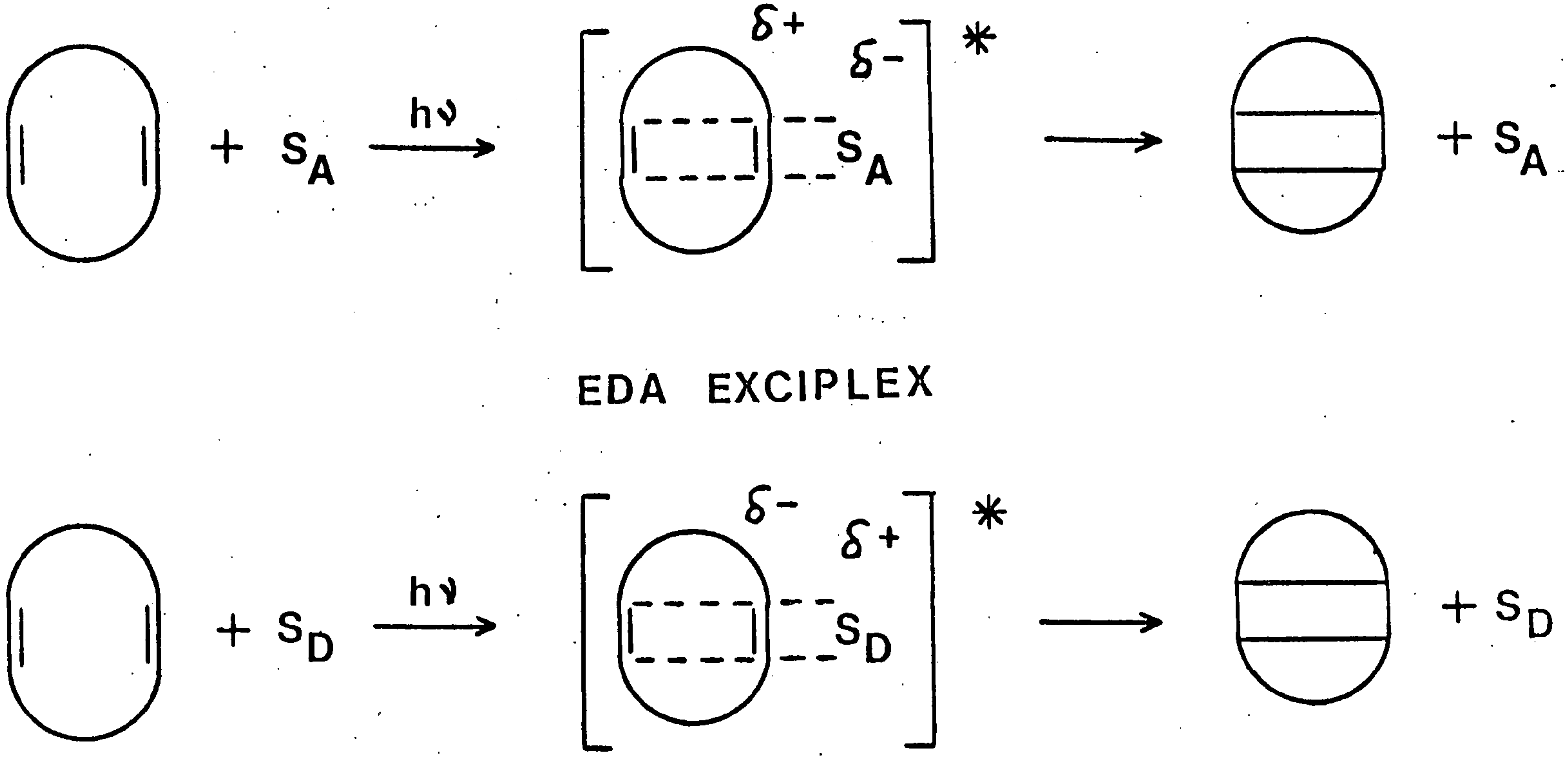
7 8

yields for these isomerizations with representative sensitizers are shown in Table I. The results for hexamethyldewarbenzene (7) are most interesting. The isomerization 7 → 8 proceeds in significant part on an excited potential energy surface (i.e., 8 is generated in a complex with sensitizer giving rise to an observable exciplex emission). The portion of ring opening which is adiabatic (that part leading to excited product, Table 1) varies among the sensitizers and depends on the excitation energy of the exciplex product (i.e., the amount of chemical potential energy which is stored during isomerization). An electron acceptor derivative of 7, a dewarphthalate, has been found to undergo exciplex isomerization although, in this case, reaction is not adiabatic providing a valuable comparison of structural requirements.

Examination of substrates which undergo exciplex isomerization and those which do not reveals several characteristics of mechanism. The sensitizer acts as a template (Scheme 1, ring closure isomerization) which polarizes electron density in quencher. If partial electron donation or withdrawal from the quencher results in changes in bond order then ring opening or closing will be favored. An additional requirement for efficient sensitized isomerization is the accessibility of a surface leading to product isomer on which excited complexes deposit polarized quencher molecules.

Biacetyl, a visible absorbing diketone, was investigated as a sensitizer and a reagent for cycloaddition with other unsaturated systems. Rates of quenching of biacetyl fluorescence and phosphorescence by alkenes and other substrates are consistent with an exciplex mechanism. Photoaddition of biacetyl to substrate, the general result of emission quenching, has been studied in detail, including the determination of quantum yield and stereochemistry of photoadducts, and the assignment of biacetyl excited state responsible for reaction.

Scheme 1



A communication describing the exciplex isomerization of 7 has appeared,[1] and a full paper including much additional data is now in preparation. The study of isomerization of quadricyclene (2) and related compounds is submitted,[2] and a thesis describing these and other exciplex systems has been completed.[3] A paper concerning biacetyl emission quenching has appeared,[4] and a full paper describing this work submitted.[5]

Charge-transfer (CT) complex systems. The exciplex-template mechanism of valence isomerization may be adopted for the photochemistry of charge transfer complexes in which a sensitizing agent is complexed in the ground state. Certain efficiencies are to be gained by precomplexation of sensitizers and isomerizable substrates. (1) Radiative or non-radiative decay of isolated excited sensitizer is eliminated. (2) Poorly absorbing sensitizers and quenchers in combination provide visible absorption properties. (3) A geometry which is likely to be appropriate for exciplex binding and the polarization which induces cycloaddition (cycloreversion) is reached prior to excitation. Suitable irradiation of the long wavelength CT band transforms a weakly bonded complex into a highly polarized complex in which the components are tightly bound.[6] (4) CT complexation could provide an affinity for supported sensitizers in heterogeneous systems.[7]

Since the photochemistry of organic charge-transfer complexes has not been reported extensively,[8] we have initiated a general investigation involving a variety of donor-acceptor pairs. We have found,[9] for example, that chloranil, a powerful quinone oxidant, complexes readily with a variety of aromatics and conjugated dienes resulting in new CT absorption bands in the visible. Irradiation of these bands generally gives complex mixtures, but in a number of cases photoproducts have been identified. The most general result is the observation of efficient photoreduction of chloranil to its hydroquinone

Table 1. Quantum Yield Data for Exciplex Isomerization in Non-polar Solvent

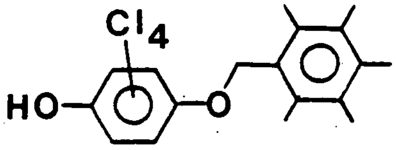
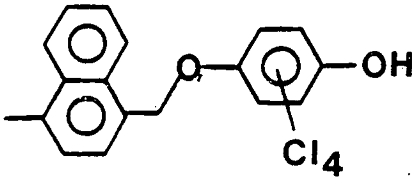
Isomerization Observed	Fluorescent Sensitizer	Limiting Quantum Yield
2 → 1	1-cyanonapthalene	0.71
	anthracene	0.65
	biacetyl	0.27
4 → 3	9,10-dicyanoanthracene	0.28
3 → 4	2-methoxynathalene	0.30
	chrysene	0.20
5 → 6	1-cyanonaphthalene	1.0
	9,10-dicyananthracene	0.14
7 → 8	1-cyanonaphthalene	0.98 (20%)[a]
	terphthalonitrile	1.0 (32%)[a]
	9,10-dicyanoanthracene	0.98 (50%)[a]

[a] Percentages refer to portion of exciplex isomerization which is adiabatic.

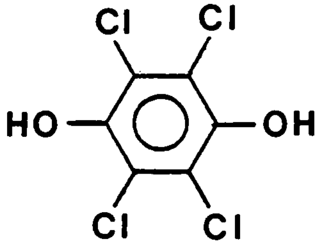
derivative in competition with the formation of ethers through photoaddition. In Table II are shown CT absorption data and product structures.

Photolysis of CT bands resulting in valence isomerization of one of the CT complex components has been observed for the first time. Thus, a complex of 2 with fumaronitrile gave 1 with Ø = 0.2; similarly, combination of 7 and fumaronitrile on photolysis gave 8 with Ø = 0.4. Fumaronitrile is an alkene capable of geometrical isomerization. This reaction did not accompany valence isomerization of 7, a result which excludes a possible mechanistic path for exciplex isomerization involving covalent bonding between donor and acceptor.

Table 2. Charge-transfer Absorption Maxima and Products from CT Irradiation of Chloranil and Alkene or Aromatic Donors

Donor	λ_{max}(nm)	Yield of Hydroquinone[a]	Other Product
2,5-dimethyl-2,4-hexadiene	562	52%	
2,5-dimethylfuran	511	69%	
1,3-cyclohexadiene	480	84%	
1,4-napthoquinone	543	69%	
acenaphthene	555	68%	
hexamethylbenzine	510	12%	
1,4-dimethylnaphthalene	536	--	

[a] Hydroquinone product:



Energy transfer systems. The photoisomerization of 3 induced by transfer of excitation energy from triplet photosensitizers has been previously reported.[10] The reaction, 3 → 4 stores a significant amount of photon energy (Δ H = 19 kcal/mol) as chemical potential energy in a kinically stable molecule. The issue which we wish to resolve for this important prototype involves setting the lower limit for the excitation energy in triplet sensitizer which is sufficient for reaction with a reasonable efficiency. This determination will in part reveal just how far into the visible the action spectrum for photosensitized isomerization will extend.

The triplet level of 3 cannot be precisely located since the molecule does not phosphoresce. However, the profile of isomerization quantum yield and concentration of 3 varies with sensitizer depending on whether triplet energy transfer is exothermic. Figure 1 shows the trend of data which allows assignment of the triplet level for 3 of about 53 kcal/mol when the lifetimes of the sensitizers are taken into account.

Sensitization of 3 → 4 using a modest triplet donor (E_T= 47 kcal/mol) would would seem to be perilous. However, just such a low energy sensitizer, benzanthrone, is effective in driving the reaction. The isomerization quantum yield is modest at ambient temperature, but on raising the temperature to 90° the sensitized reaction becomes relatively efficient. This temperature dependence of quantum yield is shown in Figure 2. From extensive measurements of concentration and temperature dependence of isomerization of 3 (Fig 3) we have been able to calculate an "activation energy" for energy transfer of 6.5 kcal/mol, a figure which agrees well with the endothermicity of excitation transfer. Rate constants for quenching of benzanthrone triplets range from 0.3×10^4 to 1.2×10^5 $M^{-1}sec^{-1}$ for temperatures between 5 and 92°. The "upconversion" of excitation energy is possible because triplet sensitizers are long lived

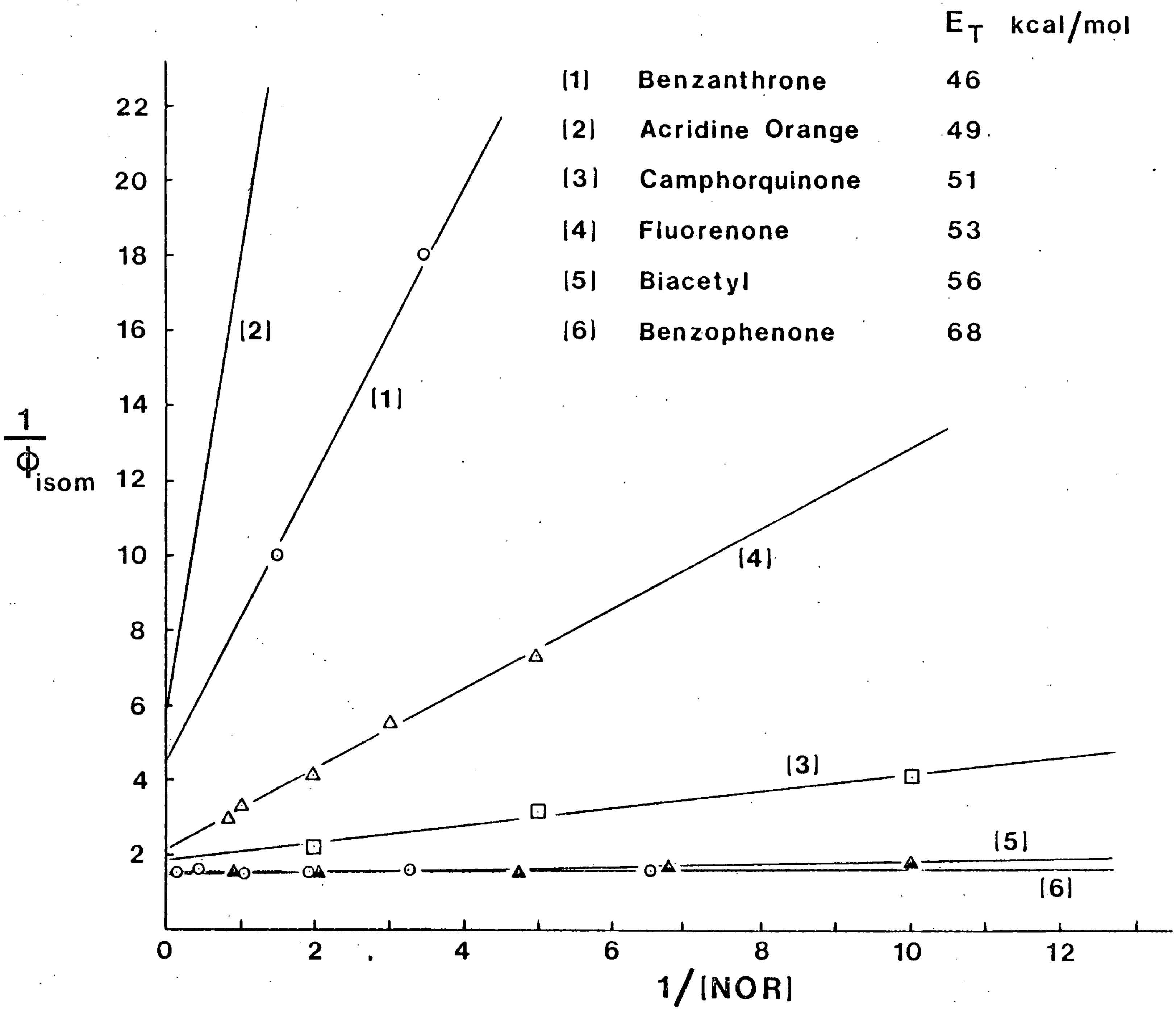
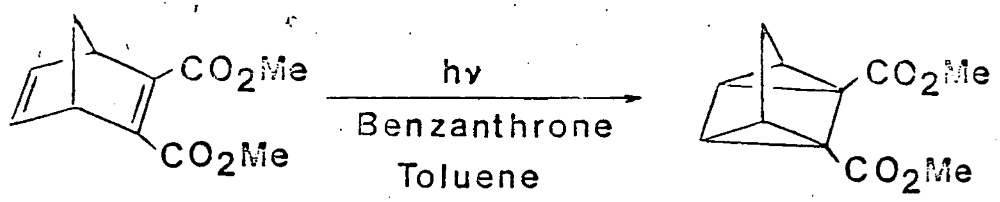


Figure 1. Quantum Yields of isomerization, 3 → 4, as a function of [3] for various sensitizers



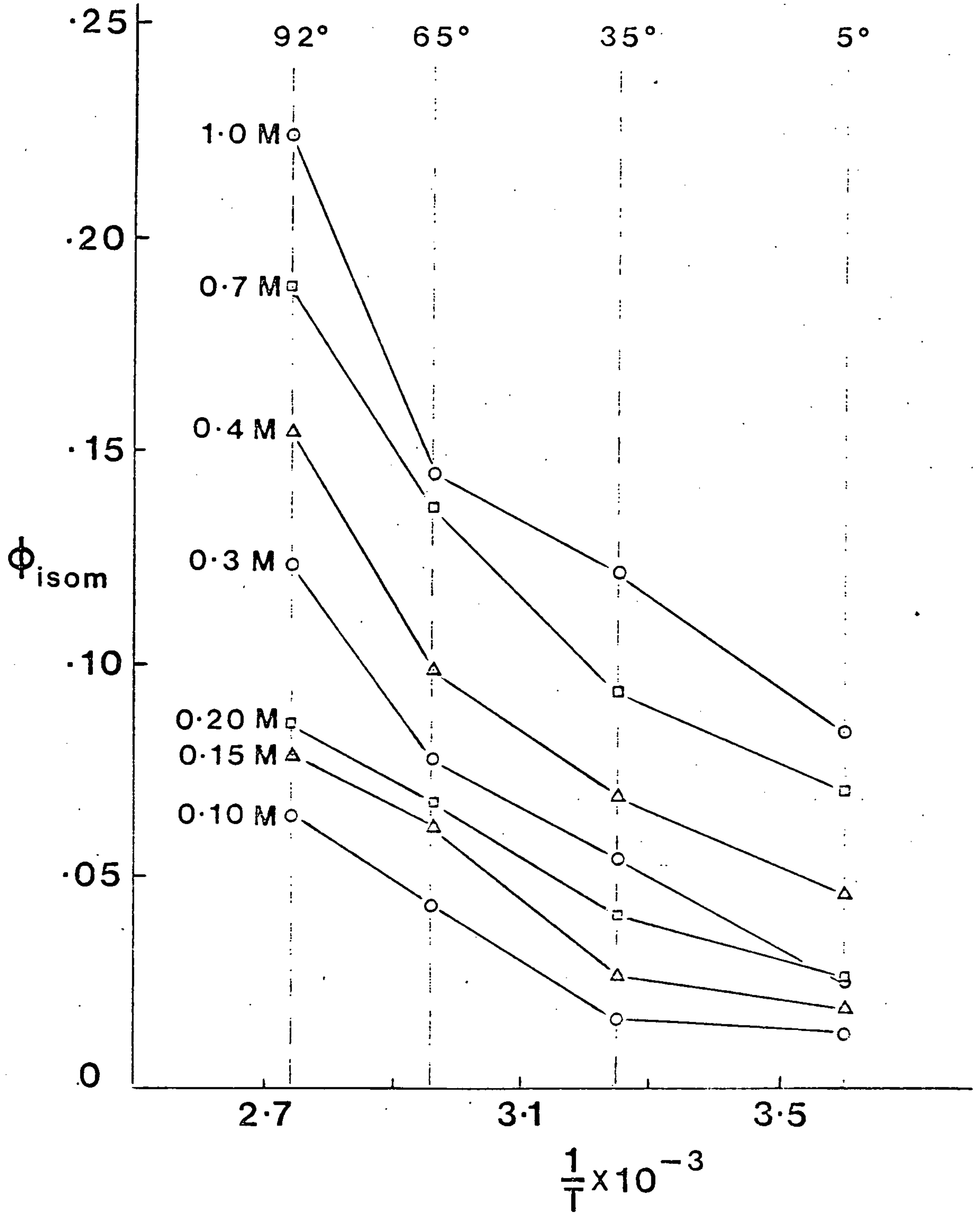


Figure 2. Quantum yields of isomerization, $\underline{3} \rightarrow \underline{4}$, as a function of temperature and concentration of $\underline{3}$.

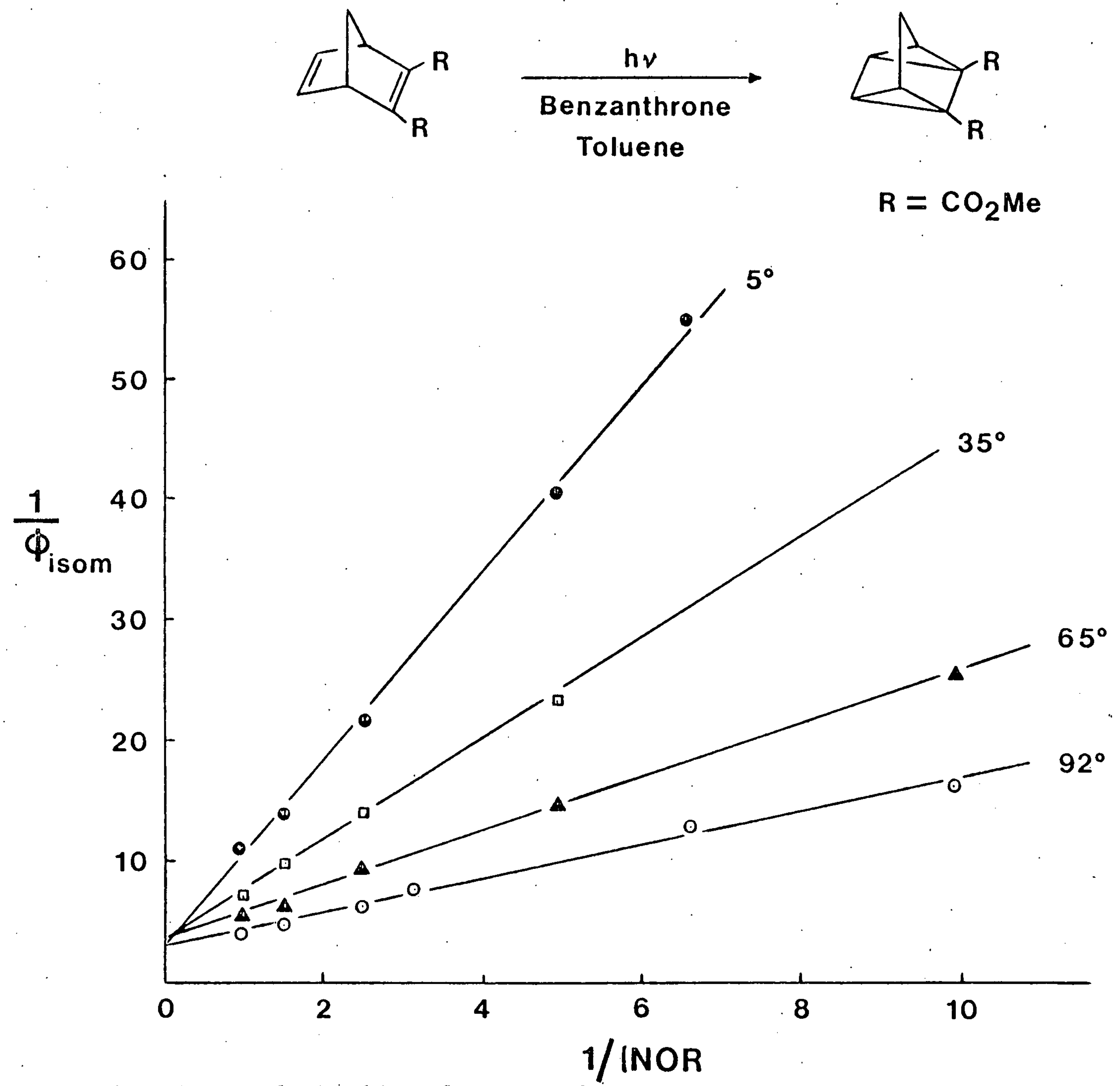


Figure 3. Linear relationships of reciprocal quantum yield and reciprocal quencher concentration for isomerization of 3 at various temperatures.

providing many encounters with quencher molecules the most energetic of which allow energy transfer. Reverse energy transfer is not important if a very rapid isomerization reaction depletes quencher triplets.

The photosensitization of 3 → 4 by benzanthrone is remarkable in that a 46 kcal/mol triplet is successful in driving a reaction which stores nearly half that energy. The temperature dependence of reaction quantum yield is the key element in achieving this result. The upgrading of low quantum yields for photoreactions which utilize low energy excited species would be of general importance and we intend to pursue the matter with a study of a number of systems including those related to reaction of 3.

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(4) G. Jones, II, M. Santhanam, and S.-H. Chiang, J. Photochem., 12, 267 (1980).

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(9) G. Jones, II, X.T. Phan, W.G. Becker, S. Kanoktanaporn, and J. Brunner, unpublished results.

(10) G. Jones, II, S.-H. Chiang, and P.T. Xuan, J. Photochem., 10, 1 (1979).

PUBLICATIONS AND PRESENTATIONS CITING DOE SUPPORT

Publications

(1) G. Jones, II, S.H. Chiang, and P.T. Xuan, "Energy Storage in Organic Photoisomers," J. Photochem., 10, 1 (1979).

(2) G. Jones, II, P.T. Xuan, and S.H. Chiang, "Chemical Conversion and Storage of Solar Energy," R.B. King, C.R. Kutal, and R.R. Hautala, Ed., The Humana Press, Inc. Clifton, N.J., 1979.

(3) G. Jones, II, and S.H. Chiang, "Exciplex Isomerization of Dewar Benzenes. Factors Controlling Diabatic and Adiabatic Reaction Paths," J. Am. Chem. Soc., 101, 7421 (1979).

(4) G. Jones, II, M. Santhanam, and S.H. Chiang, "The Quenching of Biacetyl Phosphorescence by Alkenes: A Dissection of Rate Effects on Exciplex Formation and Exciplex Decay for Ketone Triplet Quenching," J. Photochem., 12, 267 (1980).

(5) G. Jones, II, S.H. Chiang, W.G. Becker, and D.P. Greenberg, "Structure-Reactivity Factors for Exciplex Isomerization of Quadricyclene and Related Compounds," J.C.S. Chem. Comm., in press.

(6) G. Jones, II, M. Santhanam, and S.H. Chiang, "Photoaddition of Biacetyl and Alkenes. Reaction Stereochemistry, Multiplicity, and Photokinetics," J. Am. Chem. Soc., submitted.

Thesis

Sheau-Hwa Chiang, "Valence Isomerization of Electron Donor-acceptor Exciplexes," Ph.D. Dissertation, Boston University, 1979.

PRESENTATIONS:

(1) Invited lecture: G. Jones, II, "Exciplex Isomerization - Generality and Potential for Photochemical Energy Storage," Symposium on Nonbiological Photochemical Conversion and Storage of Solar Energy, 8th Northeast Regional Meeting of the American Chemical Society, Boston, MA, June, 1978, Abstract PHYS 13.

(2) Plenary lecture: G. Jones, II, S.H. Chiang, and P.T. Xuan, "Energy Storage in Organic Photoisomers," Second International Conference on the Photochemical Conversion and Storage of Solar Energy," Cambridge, England, August, 1978.

(3) Invited lecture: G. Jones, II, "Photosensitization Mechanisms for Energy Storing Isomerizations," Symposium on Solar Energy, 30th Southeastern Regional Meeting of the American Chemical Society, Savannah, GA, November, 1978, abstract 401.

(4) Invited lecture: G. Jones, II, "Energy Storing Organic Photoreactions," The Technical Forum, Photochemistry Chapter, 3M Company, Saint Paul, MN, December 20, 1978.

(5) Contributed paper: G. Jones, II and S.H. Chiang, "Diabatic and Adiabatic Exciplex Isomerization, American Chemical Society - Chemical Society of Japan Chemical Congress, Honolulu, Hawaii, April, 1979, abstract ORGN 155.

(6) Invited lecture: G. Jones, II, "Photosensitized Energy Conversion: Exciplex and Energy Transfer Routes," Gordon Research Conference on Organic Photochemistry, Proctor Academy, Andover, NH, July, 1979.

MANAGEMENT REPORT

For the current contract which began on July 1, 1979, the principal investigator is committed to 20% of time during the academic year and one summer month. Additional personnel include Dr. X.T. Phan, a postdoctoral who has worked on the project since October, 1977 (to September, 1979), and Dr. W. Schwarz (Ph.D., ETH, Zurich) who arrived in October to assume full time duties. A graduate student, Sheau-Hwa Chiang, completed work for the Ph.D. in June, 1979 and stayed on as a postdoctoral associate through December, 1979. She now has a postdoctoral position at Princeton University. Graduate students currently conducting DOE related research are W.G. Becker (M.S., Depaul University) (now supported full time) and R. Butler (B.S., SUNY, Albany), and T.-J. Chen, (B.S., National Taiwan University).

Contract funds remaining on January 31, 1980 were $33,433.75. These funds will be expended by the end of the contract period, June 30, 1980. Capital equipment purchased under the contract (December, 1979) consisted of a Perkin-Elmer Model 552 Scanning UV-VIS Spectrophotometer with recorder and accessories ($8132).