Competing Reactions of Electronically Excited 1,3-Trimethylene Dicinnamate

J. Rennert,* S. Soloway, I. Waltcher, and B. Leong

Contribution from the Department of Chemistry, The City College of the City University of New York, New York, N. Y. 10031. *Received April 12, 1972*

Abstract: Ultraviolet irradiation of 1,3-trimethylene dicinnamate ester in dilute cyclohexane solution has allowed us to study the efficiencies of the competing reactions of photocyclization and photoisomerization for this system. The former competes quite effectively, its efficiency being 18% of the latter.

There are two reaction pathways that may be taken by cinnamic acid and its derivatives when electronically excited by near-ultraviolet light. In liquid media, photoisomerization takes place.[1,2] When one olefinic bond of a cinnamoyl residue in the ground state is within the requisite distance for reaction with an excited cinnamoyl unit, excitation energy may be dissipated by the formation of cyclobutane derivatives. This latter case has been studied in great detail for the solid state[3] where photocyclization is the only reaction pathway. More recently, this laboratory has reported[4] that dicinnamate esters in dilute solution photocyclize to cyclobutane derivatives in good yields. Not only may this system photoisomerize, but also, as in the case of the solid state, it allows high localized concentrations of both excited and ground-state cinnamoyl species necessary for the cyclization reaction to occur. It is impossible to attain this latter condition in the case of monocinnamate ester solutions even at high ester concentrations, and photoisomerization is, therefore, the only reaction route available to such solutions. Accordingly, dicinnamate esters in dilute solution appear to provide a unique basis for a study of the competition between the isomerization and the cyclization pathways, and this paper discusses the details of such a study.[5]

Experimental Section

Ethyl *trans*-cinnamate, Eastman Organic Chemicals, was vacuum distilled at 6 Torr and the fraction boiling at 130–135° collected. 1,3-Trimethylene dicinnamate was prepared and purified as reported earlier.[4] Spectrograde cyclohexane, Fisher, was used as the solvent without further purification.

In the near-ultraviolet the absorption spectrum of polymethylene dicinnamates is due to the $C_6H_5CH{=}CHCOOCH_2$- group. Thus absorptivities determined for the isomeric ethyl cinnamates are applicable for spectrophotometric analysis of the dicinnamates. Mixtures of ethyl *cis*- and *trans*-cinnamate were prepared by photoisomerizing the *trans*-cinnamate in cyclohexane. Absorption spectra for mixtures were obtained on a Cary Model 14R spectrophotometer concomitant with gas chromatographic analysis utilizing a flame ionization detector. Cis–trans isomers were separated on a 10-ft, 10% DEGS on Chromosorb W-AW column in a Perkin-Elmer Model 881 CRS chromatograph. Thermal isomerization in the column was negligible.[6]

One-centimeter square quartz cells were used as reaction vessels and were positioned reproducibly in a light tight housing in front of the intensity monitor, a Model 65 Yellow Springs Instruments radiometer. Exciting radiation emanated from a Bausch and Lomb high intensity grating monochromater set at 278 nm.

Results and Discussion

Analytic Method. The chromatogram areas of the cis and trans cinnamate isomers gave the ratio, R, of cis/trans. The absorptivity of the cis isomer is obtained from

$$a_{\text{cis}} = \frac{1}{R}\left(\frac{A}{bC_0} - a_{\text{trans}}\right) + a_{\text{trans}}$$

where A is the measured absorbance, C_0 the total concentration of cis and trans, and b the optical path length.

The isosbestic wavelengths and the wavelengths of maximum absorptivity difference of the cis and trans isomers were located by measuring the absorbance of isomer mixtures *vs.* pure trans solutions of the same formality. At these optimum wavelengths for spectrophotometric analysis, the absorptivities of both isomers were computed and are given in Table I. The absorbance at the isosbestic point gives the total concentration of cis and trans at any time. These data coupled with absorbances at other measuring wavelengths permit computation of concentrations of cis and trans species. The concentration of the intramolecular bicyclic photoproduct, cy, is equal to one-half the decrease in concentration of the total olefin of the irradiated solution.

Table I

Wavelength, Å	Molar absorptivity, l. mol^{-1} cm^{-1} Cis	Isosbestic	Trans
2280	4.31×10^3		2.09×10^3
2440		5.78×10^3	
2710	1.20×10^4		2.12×10^4
3000	3.13×10^3		5.29×10^3
3027		3.87×10^3	
3060	1.30×10^3		5.96×10^2

$$C_{\text{cy}} = \frac{(A_{\text{isosbestic}} - A_{\text{isosbestic initial}})C_0}{2A_{\text{isosbestic initial}}}$$

The average fraction, f, of incident exciting radiation absorbed by both isomeric species during an irradiation

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[1] B. K. Vaidya, *Proc. Roy. Soc., Ser. A*, **129**, 299 (1930).

[2] H. G. Curme, C. C. Natale, and D. J. Kelley, *J. Phys. Chem.*, **71**, 767 (1967).

[3] M. D. Cohen and G. H. J. Schmidt in "Reactivity of Solids," J. H. DeBoer, Ed., Elsevier, Amsterdam, 1961, p 556.

[4] M. Freedman, Y. Mohadger, J. Rennert, S. Soloway, and I. Waltcher, *Org. Prep. Proceed.*, **1**, 267 (1969).

[5] Support for this study was provided by the National Science Foundation through its Undergraduate Research Participation Program.

[6] M. B. Hocking, *Can. J. Chem.*, **47**, 4572 (1969).

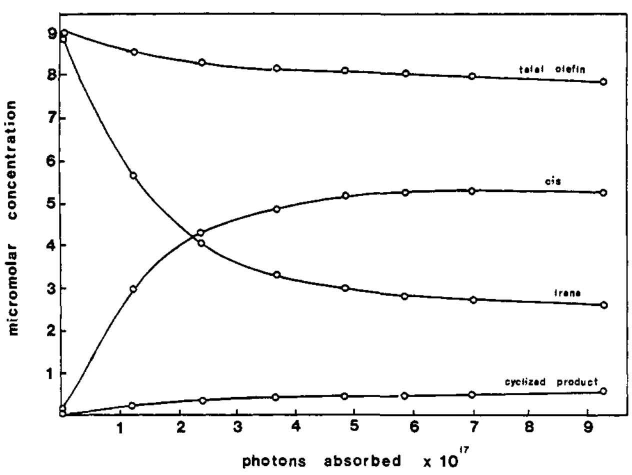

Figure 1. Plot of concentration of olefinic and cyclic species as a function of absorbed photons.

interval was obtained from the absorbances at 278 nm by

$$\bar{f} = \int_{A_1}^{A_2}(1 - 10^{-A})\mathrm{d}A \Big/ \int_{A_1}^{A_2}\mathrm{d}A$$

A fraction of this, f', is absorbed by one of the isomers, and if the average absorbance of this isomer is small, $f' = \bar{A}'/\bar{A}_{\text{total}}$ during the irradiation interval; $f'_{\text{cis}} + f'_{\text{trans}}$ is always one. Thus, the incident energy absorbed by one isomer during an irradiation interval is $\int_{t_1}^{t_2} I_0\bar{f}f'\mathrm{d}t$ where t is time and I_0 is incident intensity.

Finally, the composition of the residual dicinnamates, the trans-trans, the trans-cis, and the cis-cis, can be computed to obtain the relative quantum efficiencies of the competing photoreversible isomerization reactions and the irreversible photochemical cycloaddition reaction.

Photolysis of 1,3-Trimethylene Dicinnamate. A typical photochemical run is shown in Figure 1. The onset of irradiation causes rapid trans → cis conversion as well as intramolecular cyclization. Both reactions decelerate as the photolysis proceeds to a point where trans species is consumed by the cyclization reaction alone. The data in Table II show that the apparent quantum efficiency of the photocyclization, Φ_{cy}, decreases with reaction progress to a minimum and increases thereafter. This minimum, a quasistationary state since each of the isomers absorbs one-half of the incident radiation, is obtained in Figure 2 by locating the intersection of the extrapolated curves Φ_{cy} as a function of the cis/trans concentration ratio. It can be seen that the efficiency of cyclobutane formation decreases with increasing cis/trans concentration ratio to the minimum. This means that the quantum yield for this species is a function of the trans concentration, and that this nonradiative energy dissipating reaction takes place between the two trans moieties within the molecule TT of the following possibilities.

Table II

Concn ratio, cis/trans	Φ_{cy}	$\Phi_{\text{trans}\rightarrow\text{cis}}$
0.252	0.0746	0.404
0.809	0.0538	0.282
1.31	0.0334	0.143
1.63	0.0201	0.0837
1.83	0.0197	0.0411
1.91	0.0234	0.00758
2.00	0.0236	

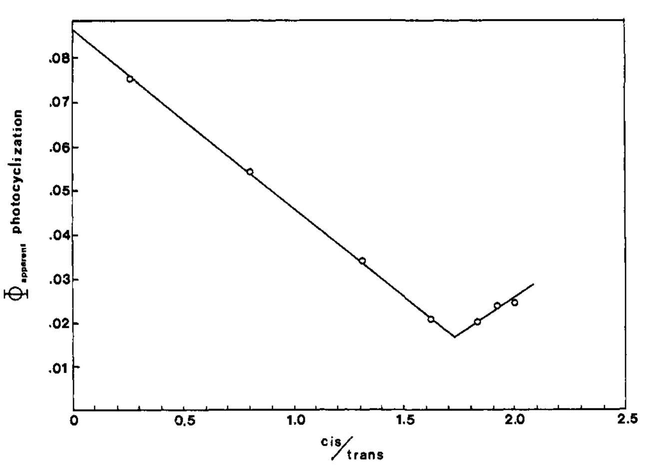

Figure 2. Plot of the apparent quantum efficiency of photocyclization as a function of the cis/trans concentration ratio.

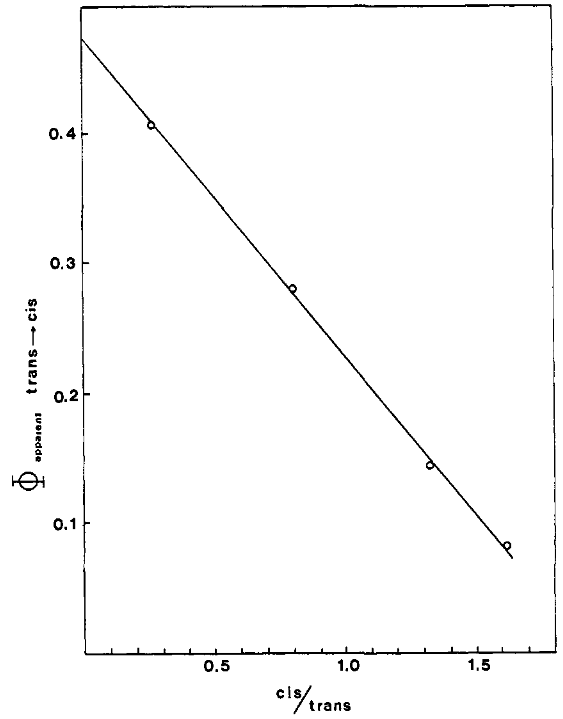

Figure 3. Plot of the apparent quantum efficiency of trans → cis cinnamate conversion as a function of the cis/trans concentration ratio.

$C_6H_5CH{=}CHCOOCH_2CH_2CH_2OOCCH{=}CHC_6H_5$

trans	trans	TT
trans	cis	TC
cis	cis	CC

This is consistent with our earlier qualitative observations[4] that the products obtained could only result from the addition reaction of two trans species.

The variation in the apparent quantum efficiency of the photocyclization reaction is ascribed to the fact that the trans–cis dicinnamate, TC, is inert with respect to the cycloaddition reaction, but the computation of the apparent quantum efficiency Φ_{cy} involves photons absorbed by trans species in both TT and TC compounds. The extrapolated quantum efficiency, where the ratio of cis/trans = 0, requires no correction since only TT is present.

The reason for the variation in the apparent quantum efficiency of the trans → cis isomerization is due to the well-known photoreversibility of this reaction.[1] The main objective of this study was to obtain relative efficiencies of the cycloaddition and the isomerization reactions. The values for the apparent quantum efficiencies of the latter as a function of cis/trans ratios are given in Table II and represented in Figure 3. The efficiency of the trans → cis isomerization is the $\Phi_{trans \rightarrow cis}$ intercept, and its value is 0.473. The extrapolated value obtained for the photocyclization is 0.086. The ratio of the efficiencies, $\Phi_{cy}/\Phi_{trans \rightarrow cis}$ is remarkably high. This is ascribed to and consistent with the concept that pairs of cinnamoyl groups have been forced into close proximity, a situation analogous to that of the solid state. The efficiency of the photocyclization reaction is approximately 18% of the value of the photoisomerization reaction. For synthetic purposes, one should be able to obtain nearly theoretical yields of cyclobutane products since the trans–trans compound is irreversibly removed from the reaction mixture, and the equilibrium is shifted toward more trans–trans formation.

Radiationless Decay of Singlet Molecular Oxygen in Solution. An Experimental and Theoretical Study of Electronic-to-Vibrational Energy Transfer

Paul B. Merkel and David R. Kearns*

Contribution from the Department of Chemistry, University of California, Riverside, California 92502. *Received January 29, 1972*

Abstract: A Q-switched ruby laser has been used to spectroscopically measure the lifetime of singlet ($^1\Delta$) oxygen in solution. The nature of the solvent is found to have a remarkable effect on the lifetime of singlet oxygen with values ranging from 2 μsec in water to 700 μsec in CCl_4. A simple theory has been developed to account for the quenching of $^1\Delta$ by the solvent in terms of intermolecular electronic-to-vibrational energy transfer. According to this theory the quenching efficiency can be quantitatively related to the intensities of infrared overtone and combinational absorption bands of the solvent in the energy regions of $^1\Delta \rightarrow {}^3\Sigma$ transitions and especially near 7880 and 6280 cm^{-1}, the respective $0 \rightarrow 0$ and $0 \rightarrow 1$ oxygen transition energies. Direct calculation of the quenching rates using this theory with no adjustable parameters yields a better than order of magnitude agreement with experimental results. An analysis of gas phase and solution quenching rate constants indicates rate constants obtained in one phase may be used to compute quenching constants in the other phase. This applies to the quenching of $^1\Sigma$ as well as $^1\Delta$. The apparent lack of a heavy atom effect on the $^1\Delta$ lifetime can be accounted for. Large deuterium effects are predicted and observed. The theory indicates that the quenching involves a second-order indirect mixing of $^3\Sigma$ and $^1\Delta$ states through $^1\Sigma$ by interaction with the solvent, in which $^3\Sigma$ and $^1\Sigma$ are mixed *via* an intramolecular spin–orbit coupling. Mixing of $^1\Sigma$ and $^1\Delta$ is also important in the quenching of $^1\Sigma$, and the matrix elements used to account for the observed quenching rate constants for $^1\Delta$ automatically lead to rate constants for the quenching of $^1\Sigma$ which are in good agreement with the experimental values. The theory thus appears to be internally consistent. The techniques used to measure the solvent-controlled decay of singlet oxygen have also been used to evaluate the absolute rate constants for the reaction of singlet oxygen with various acceptors. A quantum yield of 0.9 ± 0.1 was measured for the formation of $^1\Delta$ from quenching of triplet state methylene blue. The quenching of singlet oxygen by β-carotene and a polymethene pyrylium dye (I) has been investigated. We confirm the earlier suggestion by Foote that the β-carotene quenching of singlet oxygen is nearly diffusion controlled (2×10^{10} M^{-1} sec^{-1} in benzene). The rate constant for the quenching of $^1\Delta$ by I is found to be 3×10^{10} M^{-1} sec^{-1} in acetonitrile. The discrepancy between our observation that the lifetime of $^1\Delta$ is extremely solvent sensitive and earlier indications that the lifetime is relatively solvent independent is resolved. Our findings indicate the factors which may permit $^1\Delta$ lifetimes of greater than 1 msec in appropriate solvents to be obtained.

Recognition of the importance of singlet molecular oxygen as an intermediate in the photooxidation of unsaturated hydrocarbons has stimulated much of the current interest in the chemical and physical properties of this species.[1-4] One of the most common methods of generating singlet oxygen is *via* energy transfer from an excited triplet sensitizer to ground-state oxygen. With sensitizers having a lowest triplet state above 13,100 cm^{-1}, both $^1\Sigma$ and $^1\Delta$ oxygen are produced.[5-9] However, for solution-phase reactions

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(1) C. S. Foote and S. Wexler, *J. Amer. Chem. Soc.*, **86**, 3879 (1964).

(2) E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3881 (1964).

(3) K. Gollnick, *Advan. Chem. Ser.*, No. 77, 78 (1968).

(4) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

(5) K. Kawaoka, A. U. Khan, and D. R. Kearns, *J. Chem. Phys.*, **46**, 1842 (1967).

(6) C. K. Duncan and D. R. Kearns, *ibid.*, **55**, 5822 (1971).

(7) D. R. Kearns, A. U. Khan, C. K. Duncan, and A. H. Maki, *J. Amer. Chem. Soc.*, **91**, 1039 (1969).

(8) E. Wasserman, V. J. Kuck, W. M. Delevan, and W. A. Yager, *ibid.*, **91**, 1040 (1969).

(9) E. W. Abrahamson, *Chem. Phys. Lett.*, 10, 113 (1971).