

PHOTOISOMERIZATION OF ETHYL CINNAMATE IN DILUTE SOLUTIONS

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Summary

The quantum yields for the elementary steps of photoisomerization of ethyl cinnamate in dilute solutions (about 10^{-5} M) were determined by combining direct irradiation and irradiation sensitized with Michler's ketone at 30 °C. The quantum yields $\Phi(\text{cis} \rightarrow \text{trans})$ and $\Phi(\text{trans} \rightarrow \text{cis})$ for the overall photoisomerization are 0.26 and 0.29 respectively in ethanol and the sum of these values is much smaller than unity, indicating the existence of direct deactivation of the excited singlet state of each isomer without passing through a twisted singlet state. The fractions $\Phi_{1m}\alpha$ and $\Phi_{1m}\beta$ of each excited singlet state which is directly deactivated into the same isomeric form are 0.47 for ${}^1C_t^*$ and 0.39 for ${}^1C_c^*$, and the fraction $\delta({}^3C^* \rightarrow C_c)$ of twisted triplet state which is deactivated into the *cis* form is 0.54.

1. Introduction

Much work has been reported on photochemical *cis-trans* isomerizations and their mechanisms [1 - 3]. Twisted singlet and triplet states have been proposed as possible intermediates for the photoisomerization of stilbene [1]. For cinnamates, the excited triplet states for both isomers are supposed to be deactivated mainly through the same single twisted form with an energy minimum (twisted triplet ${}^3P^*$) [4, 5]. However, the possibility of direct deactivation without isomerization from the excited singlet state of each isomer in addition to the deactivation through the twisted singlet ${}^1P^*$ shown in Fig. 1 cannot be excluded.

The sum of the quantum yields for *trans* \rightleftharpoons *cis* photoisomerizations of cinnamic acid was found to be about unity in cyclohexane and in water (pH 2), but about 0.5 in complexing solvents such as ether and dimethyl sulphoxide [6]. Ishigami *et al.* [2] have reported the marked multiplicity

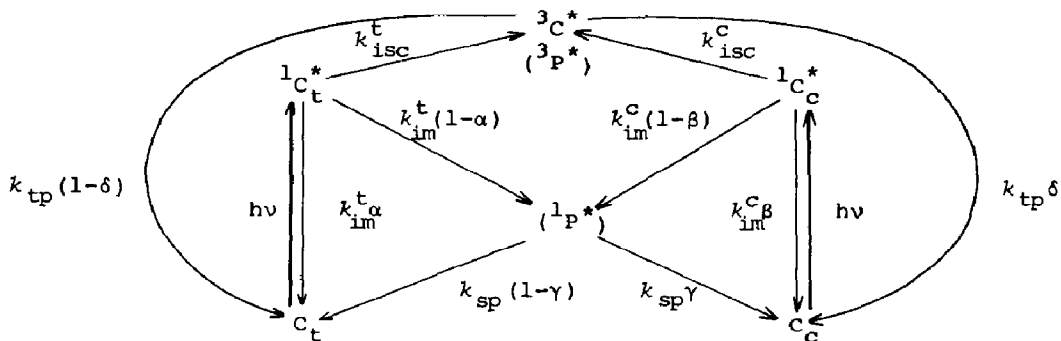


Fig. 1. Isomerization scheme of ethyl cinnamate.

dependence in the direct *trans* \rightarrow *cis* photoisomerization of *para*-substituted methyl cinnamate.

Our preliminary results [7] have shown the occurrence of photodimerization of ethyl cinnamate as well as photoisomerization in dilute ethanol solution. In the present paper the estimation of the quantum yields for the direct and sensitized photoisomerization of ethyl *trans*-cinnamate in dilute solutions is considered.

2. Experimental details

2.1. Materials

Ethyl *trans*-cinnamate (reagent grade) was vacuum distilled and the fraction boiling in the range 117 - 118 °C at 5 mmHg was collected for use. Spectrograde solvents were used without further purification after it had been checked that their absorbance was suitable for spectrophotometric use. Michler's ketone (4,4'-bis(dimethylamino)benzophenone) was recrystallized several times from methanol.

2.2. Apparatus

Sample solutions (4 ml) in a degassed and sealed rectangular quartz cell (path length $l = 1.0$ cm) were set in a thermostatted bath (30 °C). A 450 W high pressure mercury lamp (Ushio UM-452) with a stabilized power supply was used as a radiation source throughout. The mercury emission was isolated with filters of Toshiba UV-27 and UV-D33S for direct irradiation and with UV-D36A for irradiation sensitized with Michler's ketone. Chemical actinometry was performed with a potassium ferrioxalate-*o*-phenanthroline system.

2.3. UV absorption measurements

The absorption spectra during irradiation were recorded with a Shimadzu MPS-5000 spectrophotometer. The change in the concentrations $[C_t]$ and $[C_c]$ of the *trans* and the *cis* isomers respectively was evaluated from the changes in the optical densities at the isosbestic point (250 nm) and at the

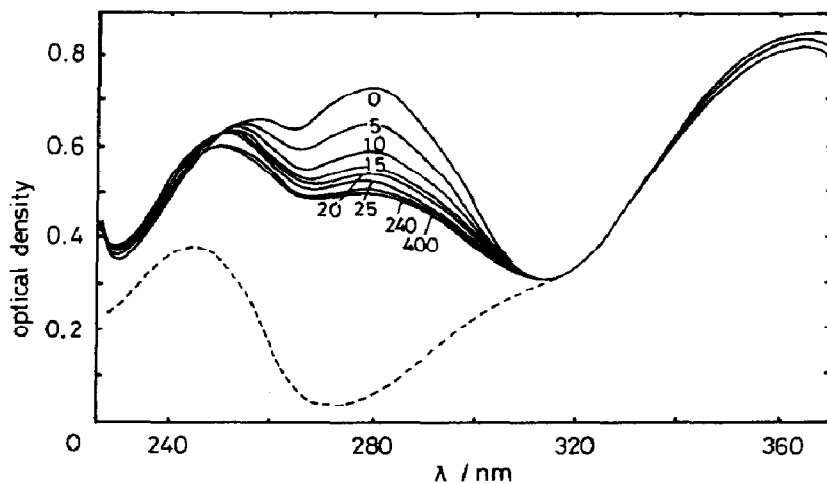


Fig. 2. UV spectra of Michler's ketone (---) and of ethyl cinnamate sensitized with Michler's ketone (—) in degassed ethanol at 30 °C. The numerals on the curves indicate the irradiation times in minutes.

maximum wavelength (276 nm) by using equations reported previously [7]. Since the cinnamate absorption peak at 276 nm does not overlap the absorption of Michler's ketone, as shown in Fig. 2, changes in the UV absorption of the cinnamates can be used to monitor the sensitized cinnamate reactions.

3. Results and discussion

3.1. Direct photoisomerization

The changes in the mole fractions of the *trans* and *cis* isomers during direct irradiation in ethanol are shown in Fig. 3. The equilibrium fraction $[C_c]_e / ([C_c]_e + [C_t]_e)$ of the *cis* isomer is about 0.69, and oxygen had no influence either on the equilibrium isomer composition (also equal to 0.69) or on the rate of photoisomerization.

By assuming stationary states for $[^1C_t^*]$, $[^1C_c^*]$, $[^1P^*]$ and $[^3C^*]$ in Fig. 1, we obtain

$$\frac{d[C_t]}{dt} = -\frac{d[C_c]}{dt} = -A[C_t] + B[C_c] \quad (1)$$

with

$$A = I_0 \epsilon_t' f_t \Phi(\text{trans} \rightarrow \text{cis}) \\ = I_0 \epsilon_t' f_t \{1 - \Phi_{im}^t \alpha - \Phi_{im}^t (1 - \alpha)(1 - \gamma) - \Phi_{isc}^t (1 - \delta)\} \quad (2)$$

$$B = I_0 \epsilon_c' f_c \Phi(\text{cis} \rightarrow \text{trans}) \\ = I_0 \epsilon_c' f_c \{\Phi_{im}^c (1 - \beta)(1 - \gamma) + \Phi_{isc}^c (1 - \delta)\} \quad (3)$$

where $\Phi_{im}^t = k_{im}^t / (k_{im}^t + k_{isc}^t)$ and $\Phi_{im}^c = k_{im}^c / (k_{im}^c + k_{isc}^c)$, ϵ' is the molar extinction coefficient at the irradiation wavelength multiplied by 2.3, I_0 is the incident photon flux and $f = (1 - 10^{-\epsilon[C]_0^l}) / 2.3\epsilon[C]_0^l$ is the correction

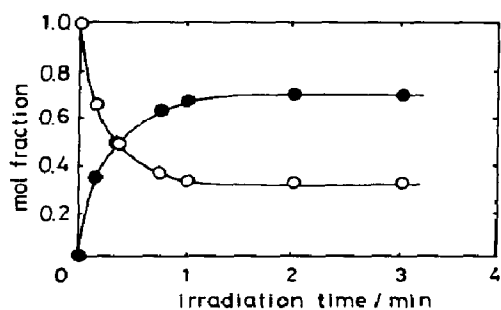


Fig. 3. Simultaneous process of *trans*-*cis* isomerization of ethyl *trans*-cinnamate (O) and ethyl *cis*-cinnamate (●) in degassed ethanol (3.03×10^{-5} M) at 30 °C.

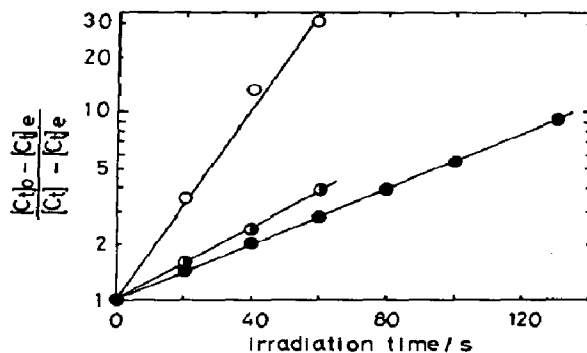


Fig. 4. First-order plots for isomerization of ethyl cinnamate in degassed solutions at 30 °C: O, ethanol; ●, tetrahydrofuran; ●, dichloroethane.

factor for the absorbed dose. The subscripts *t* and *c* denote *trans* and *cis* forms respectively.

When photoisomerization is started from the pure *trans* isomer, $[C_c] = [C_t]_0 - [C_t]$. At a later stage an equilibrium is reached ($d[C_t]/dt = 0$) and the equilibrium isomer composition $[C_t]_e$ is related to parameters *A* and *B* by

$$\frac{[C_t]_0}{[C_t]_e} = 1 + \frac{A}{B} \quad (4)$$

Hence integration of eqn. (1) gives

$$\frac{[C_t]_e}{[C_t]_0} \ln \left(\frac{[C_t]_0 - [C_t]_e}{[C_t] - [C_t]_e} \right) = Bt \quad (5)$$

A semilogarithmic plot of $([C_t]_0 - [C_t]_e)/([C_t] - [C_t]_e)$ against the irradiation time *t* according to eqn. (5) was found to be linear as shown in Fig. 4. From the slope of this straight line, the values of *B* and $\Phi(cis \rightarrow trans)$ were calculated and are summarized in Table 1. The values of *A* and $\Phi(trans \rightarrow cis)$ obtained from eqns. (4) and (2) are also given in Table 1. The quantum yields are independent of the initial concentration (10^{-5} - 10^{-4} M) of ethyl cinnamate. The sum of $\Phi(cis \rightarrow trans)$ and $\Phi(trans \rightarrow cis)$ is much less than unity (about 0.55) and is comparable with the reported results for cinnamic acid measured in complexing solvents [6] and suggests the existence of direct deactivation without isomerization from the excited singlet state of each isomer. The presence of oxygen did not affect the quantum yields for *cis* \rightarrow *trans* and *trans* \rightarrow *cis* isomerization, e.g. $\Phi(cis \rightarrow trans) = 0.25$ and $\Phi(trans \rightarrow cis) = 0.27$ in ethanol in the presence of oxygen.

Since the equilibrium isomer composition depends on ϵ_t' and ϵ_c' as is assumed from eqns. (2) - (4), as well as on the solvent viscosity [8] or the polarity [9], the equilibrium isomer composition is influenced by the nature of the solvent (Table 1).

TABLE I

Cis-trans equilibrium isomer composition and quantum yields for isomerization of ethyl cinnamate in degassed solutions at 30 °C

<i>Solvent</i>	$[C_t]_0$ ($\times 10^{-5}$ M)	$[C_c]_e / ([C_t]_e + [C_c]_e)$	B ($\times 10^{-2}$ s $^{-1}$)	$\Phi(\text{cis} \rightarrow \text{trans})$	A ($\times 10^{-2}$ s $^{-1}$)	$\Phi(\text{trans} \rightarrow \text{cis})$
Ethanol	3.03	0.69	1.6	0.25	3.6	0.27
	7.81	0.69	1.8	0.27	3.9	0.30
Dichloroethane	3.04	0.63	0.63	0.13	1.1	0.083
Tetrahydrofuran	3.02	0.57	0.95	0.15	1.3	0.098

3.2. Sensitized photoisomerization

Ethyl *trans*-cinnamate, sensitized with 2.69×10^{-5} M of Michler's ketone at 365 nm, showed a rapid *trans* \rightarrow *cis* photoisomerization followed by photodimerization in degassed ethanol solution as is shown in Fig. 2.

By using stationary state approximations for $[^3P^*]$ and $[^3MK^*]$, we obtain

$$\ln\left(\frac{[C_t]_0 - [C_t]_e}{[C_t] - [C_t]_e}\right) = Dt \quad (6)$$

with

$$D = \frac{I_0 \epsilon_{MK} f_{MK} \phi_{et} [MK]_0}{[C_t]_0} \quad (7)$$

$$\phi_{et} = \frac{k_{et}^t [C_t] + k_{et}^c [C_c]}{k_{et}^t [C_t] + k_{et}^c [C_c] + k_{it}^{MK}} \quad (8)$$

(MK \equiv Michler's ketone) where ϕ_{et} is the quantum yield of energy transfer from $^3MK^*$ to cinnamate, k_{it}^{MK} is the rate constant for triplet decay of $^3MK^*$ and k_{et} is the rate constant for energy transfer from $^3MK^*$ to ethyl cinnamate. The equilibrium isomer composition for the condition of $d[C_t]/dt = 0$ is given by

$$\frac{[C_c]_e}{[C_t]_0} = 1 - \frac{[C_t]_e}{[C_t]_0} = \frac{\delta k_{et}^t}{\delta k_{et}^t + (1 - \delta) k_{et}^c} \quad (9)$$

A semilogarithmic plot according to eqn. (6) (Fig. 5) gives ϕ_{et} to be about 6×10^{-3} by using eqn. (7) and with the assumption that $k_{et}^t = k_{et}^c = k_{et}$ which is justified by the same phosphorescence spectra of *trans*- and *cis*-cinnamic acid in ether-isopentane-ethyl alcohol glass [4]. The low efficiency of energy transfer ($k_{et} \approx 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ from eqn. (8) together with $k_{it}^{MK} = 2.0 \times 10^5 \text{ s}^{-1}$ in ethanol [10]) may be attributed to the small difference in the triplet energy levels for ethyl cinnamate ($E_T = 64 \text{ kcal}$

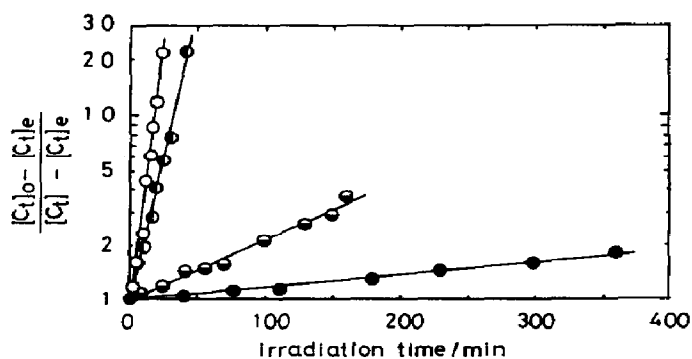


Fig. 5. First-order plots for the sensitized isomerization of ethyl cinnamate in ethanol irradiated at 365 nm: O, $[C] = 3.24 \times 10^{-5}$ M, $[MK] = 2.69 \times 10^{-5}$ M (in vacuum); ⊙, $[C] = 10.3 \times 10^{-5}$ M, $[MK] = 2.69 \times 10^{-5}$ M (in vacuum); ⊖, $[C] = 3.24 \times 10^{-5}$ M, $[MK] = 2.69 \times 10^{-5}$ M (in air); ●, $[C] = 3.24 \times 10^{-5}$ M, $[MK] = 0$ (in vacuum).

TABLE 2

Cis-trans equilibrium isomer composition and quantum yields for isomerization of ethyl cinnamate sensitized with Michler's ketone in degassed ethanol at 30 °C

$[C_t]_0$ ($\times 10^{-5}$ M)	$[MK]_0$ ($\times 10^{-5}$ M)	$[C_c]_e /$ $([C_t]_e + [C_c]_e)$	δ	D ($\times 10^{-3}$ s $^{-1}$)	ϕ_{et}
3.24	2.69	0.55	0.55	2.2	0.0039
5.41	2.69	0.53	0.53	2.0	0.0058
10.3	2.69	0.53	0.53	1.1	0.0062
3.24	0	0.49		0.024	

TABLE 3

Quantum yields for various elementary processes in isomerization of ethyl cinnamate in ethanol at 30 °C

$\Phi_{im} \approx 0.62$
$\Phi_{isc} \approx 0.38$
$\Phi(cis \rightarrow trans) = 0.26$
$\Phi(trans \rightarrow cis) = 0.29$
$\alpha(^1C_t^* \rightarrow C_t, \text{direct}) = 0.76$
$\beta(^1C_c^* \rightarrow C_c, \text{direct}) = 0.63$
$\delta(^3C^* \rightarrow C_c) = 0.54$

mol $^{-1}$ for *trans*-cinnamic acid [11]) and Michler's ketone ($E_T = 62$ kcal mol $^{-1}$ [12]).

From the equilibrium isomer composition of sensitized photoisomerization, $\delta = [C_c]_e/[C_t]_0$ was estimated to be about 0.54, as shown in Table 2. The fractions α and β , which are deactivated directly to the ground state of the same isomeric form from $^1C_t^*$ and $^1C_c^*$ respectively, can be easily calculated to be 0.76 and 0.63 from eqn. (2) and eqn. (3) respectively, by using $\delta = 0.54$ together with $\Phi_{isc} = (1 - \Phi_{im}) = 0.38$ determined from the quantum yields of sensitized and unsensitized photodimerization for the same system [10], and by assuming $\gamma(^1P^* \rightarrow C_c) = \delta$. The results are summarized in Table 3. In conclusion, the present study on photoisomerization of ethyl cinnamate in dilute solutions with direct irradiation and irradiation sensitized with Michler's ketone shows that nearly half of the excited singlet state of each isomer in ethanol is directly deactivated to the ground state of the same isomer ($\Phi_{im}\alpha = 0.47$ for $^1C_t^*$ and $\Phi_{im}\beta = 0.39$ for $^1C_c^*$), while the remainder is converted to both twisted singlet and twisted triplet states.

References

- 1 J. Saltiel and J. L. Charlton, in P. de Mayo (ed.), *Rearrangements in Ground and Excited States*, Vol. 3, Academic Press, New York, 1980, p. 42.

- 2 T. Ishigami, K. Nakazato, M. Uehara and T. Endo, *Tetrahedron Lett.*, (1979) 863.
- 3 T. Arai, T. Karatsu, H. Sakuragi and K. Tokumaru, *Chem. Lett.*, (1981) 1377.
- 4 K. Nakamura and S. Kikuchi, *Bull. Chem. Soc. Jpn.*, 41 (1968) 1977.
- 5 H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, 85 (1981) 1835.
- 6 M. Bolte, C. Lorain and J. Lemaire, *C.R. Acad. Sci., Ser. II*, 293 (1981) 817.
- 7 Y. Shindo, K. Horie and I. Mita, *Chem. Lett.*, (1983) 639.
- 8 D. Gegiou, K. A. Muszkat and E. Fischer, *J. Am. Chem. Soc.*, 90 (1968) 12.
- 9 D. Schulte-Frohlinde, H. Blume and H. Gusten, *J. Phys. Chem.*, 66 (1962) 2486.
- 10 Y. Shindo, K. Horie and I. Mita, *Preprint, 3rd Technical Conf. on Photopolymers, Tokyo, 1982.*
- 11 K. Nakamura and S. Kikuchi, *Bull. Chem. Soc. Jpn.*, 40 (1967) 1028.
- 12 S. L. Murov, *Handbook of Photochemistry*, Dekker, New York, 1973, p. 3.