CHEMISTRY LETTERS, pp. 639-642, 1983. © The Chemical Society of Japan 1983

RATE FOR PHOTODIMERIZATION OF ETHYL CINNAMATE IN DILUTE SOLUTION

Yoichi SHINDO,* Kazuyuki HORIE,† and Itaru MITA†
Department of Chemistry, Faculty of Science, Toho University, Miyama,
Funabashi, Chiba 274
†Institute of Interdisciplinary Research, Faculty of Engineering,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

Kinetic parameters for photodimerization of ethyl cinnamate were determined in dilute ethanol solution ($3\sim5\times10^{-5}$M) where the spontaneous deactivations of excited states proceed much faster than their bimolecular reactions. The quantum yield of cyclodimer formation from excited singlet state, $\Phi'_{DM}/[C]_0 \simeq \tau_M k_{DM}$, and that from excited triplet state, $\Phi_{ISC}\Phi'_{DT}/[C]_0 \simeq \Phi_{ISC}\tau_T k_{DT}$, are 15 M^{-1} and 13 M^{-1}, respectively, in ethanol at 30°C.

Many works[1~10] have been reported on the photoreaction of cinnamic acid and its derivatives. Recently Egerton et al.[10] have shown that cyclodimers are obtained in high yield by the irradiation of not only solid but liquid ethyl cinnamate , which removed a serious objection[3,4] against the possibility of photocycloaddition in amorphous system. The rate constants for photodimerization of cinnamates in solution, however, have not yet been reported so far.

Since the photodimerization of ethyl cinnamate (C) is supposed to occur according to the scheme shown in Fig. 1, the quantum yield of photodimerization, Φ_D, is given by

$$\Phi_D = \Phi_{DM} + \Phi_{ISC}\Phi_{DT} \tag{1}$$

where Φ_{DM}, Φ_{DT}, and Φ_{ISC} are the quantum yields of cyclodimer (D) formation from the excited singlet ($^1C^*$) and from the triplet state ($^3C^*$) and that of intersystem crossing, respectively. Φ_{DM} is expressed by

$$\Phi_{DM} = k_{DM}[C]/(k_{IM} + k_{ISC} + k_{DM}[C] + k_{Mq}[C]) \tag{2}$$

where the rate constants are shown in Fig. 1. Thus far it has been roughly considered that the photodimerization proceeds through $^1C^*$ when cinnamate is directly irradiated, and through $^3C^*$ when a triplet sensitizer is used.[1,2,8] In bulk liquid or in concentrated solution where all the previous works[1,6,7,10] were carried out, the last two terms in the denominator, $k_{DM}[C]+k_{Mq}[C]$, in equation (2) were unable to be neglected compared with $(k_{IM}+k_{ISC})$. Therefore, Φ_{DM} is not proportional to cinnamate concentration [C], and many difficulties arise in the estimation of the kinetic parameters for photodimerization of

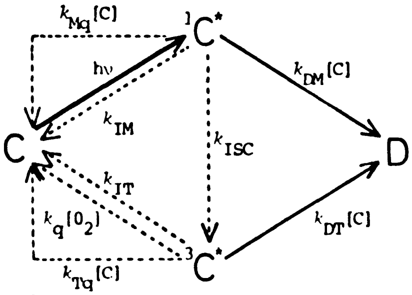

Fig. 1. Photodimerization of ethyl cinnamate.

ethyl cinnamate. In this work, we used very dilute solution ($[C]_0<10^{-4}$M) where $k_{IM}+k_{ISC} \gg k_{DM}[C]+k_{Mq}[C]$ and $k_{IT} \gg k_{DT}[C]+k_{Tq}[C]$, and the kinetic parameters for photodimerization of ethyl cinnamate were determined based on the experiments in the absence and presence of oxygen.

Ethyl *E*-cinnamate was vacuum distilled. Spectrograde solvent was used without further purification. The sample solutions ($3\sim5\times10^{-5}$M) in a degassed and sealed or an aerated rectangular quartz cell were set in a thermostat (30°C), and irradiated by a 450W high pressure mercury lamp with filters of Toshiba UV-27 and UV-D33S. Chemical actinometry was performed with potassium ferrioxalate/o-phenanthroline system.

The change in ultraviolet absorption spectra of ethyl *E*-cinnamate in ethanol is shown in Fig. 2. An isosbestic point for trans(*E*) and cis(*Z*) isomers[9] is observed at 250 nm for initial several minutes irradiation. Further irradiation results in the disappearance of the isosbestic point and the decrease in the total concentration of trans and cis isomers.

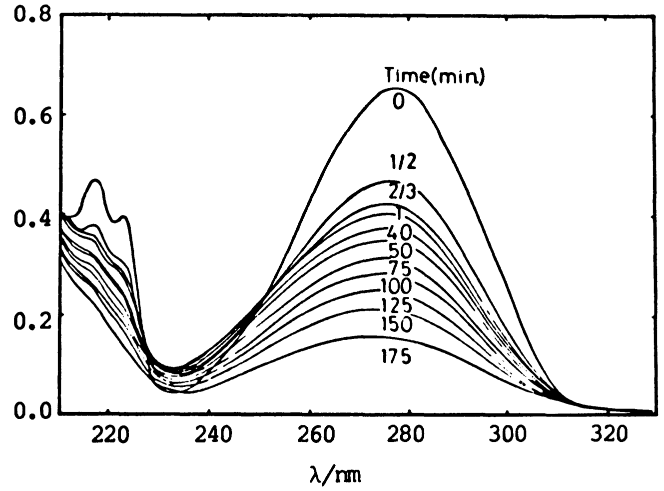

Fig. 2. UV-spectra of ethyl cinnamate in degassed ethanol (3×10^{-5}M) before and after irradiation at 30°C.

In order to identify the photoproducts obtained from ethyl *E*-cinnamate irradiated in ethanol, the solution was thoroughly irradiated for 48 hours until the absorption at 240~300 nm almost disappeared. After the removal of solvent by evaporation, the residue was analyzed by Toyōsoda GPC-802UR type gel permeation chromatograph (GPC) with G2000H8 column and UV (250 nm) detector, and Hitachi M-80A type gas chromatograph-mass spectrometer (GC-MS). The GPC elution curves with tetrahydrofuran as an elution solvent are shown in Fig. 3. The elution volume (EV) can be converted to the molecular weight by using a calibration curve shown in the insert of Fig. 3. When the dilute solution was irradiated, a peak at 33.7 ml for ethyl *E*-cinnamate disappeared and a new peak at 27.7 ml corresponding to molecular weight of 352 (dimer) appeared, but no peak in higher molecular weight region was observed. For comparison with the photoproduct in dilute solution, liquid ethyl cinnamate was spread as a thin film (about 15 μm) between two UV-27 filter plates and

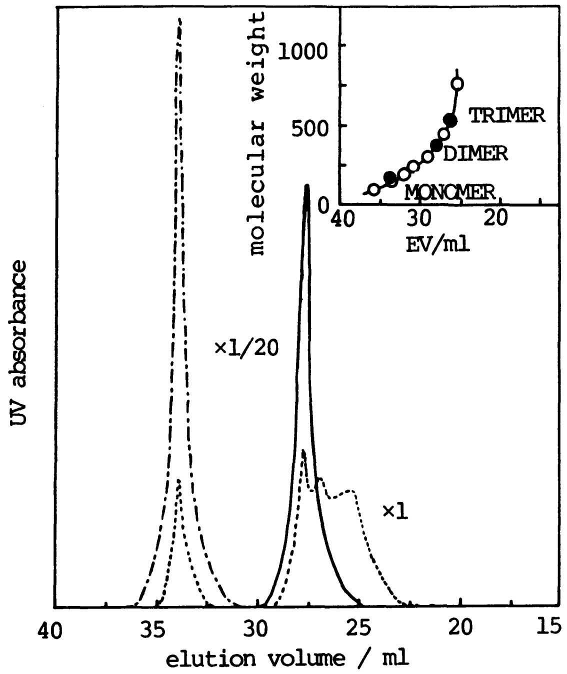

Fig. 3. GPC-elution curve of ethyl cinnamate and its photoproduct.
—·—: before irradiation
——: after irradiation in dilute solution
----: after irradiation in bulk

irradiated for 170 hours at 30°C. The sample showed both peaks at 27.7 ml and 33.7 ml in addition to other peaks corresponding to trimer and higher oligomers in accordance with the result of Egerton et al.[10)]

The time-course of the extent of photoisomerization and photodimerization was evaluated from Fig. 2 by using equations[9)]

$$[C_t]/[C_t]_0 = [\varepsilon_t/(\varepsilon_t - \varepsilon_c)][(E_2/E_{2,0}) - (\varepsilon_c E_1/\varepsilon_t E_{1,0})] \qquad (3)$$

$$[C_c]/[C_t]_0 = [\varepsilon_t/(\varepsilon_t - \varepsilon_c)][(E_1/E_{1,0}) - (E_2/E_{2,0})] \qquad (4)$$

$$[D]/[C_t]_0 = 1 - (E_1/E_{1,0}) \qquad (5)$$

where t, c, and D denote trans form, cis form, and cyclodimer. E_1 (at 250 nm) and E_2 (at 276 nm) are the optical densities, ε_t and ε_c are molar extinction coefficients of trans and cis forms at 276 nm (ε_t=21000 $M^{-1}cm^{-1}$, ε_c=9300 $M^{-1}cm^{-1}$), and subscript 0 corresponds to the initial state. The trans-cis photoisomerization attained an equilibrium after a few minutes irradiation in the present experimental conditions, and then photodimerization proceeded holding a constant isomer composition. The equilibrium fractions of the cis isomer, $[C_c]_e/[C_c]_e+[C_t]_e$, at verious conditions are listed in Table 1. The rate of the change in monomer concentration, $[C]=[C_t]+[C_c]$, is expressed by equation (6) for the present condition,

$$-d[C]/dt = (k_{DM}[C]\tau_M + \Phi_{ISC}k_{DT}[C]\tau_T)\times10^3 I_0(1 - 10^{\varepsilon[C]l})/l \qquad (6)$$

where $\tau_M=1/(k_{IM}+k_{ISC})$ and $\tau_T=1/k_{IT}$ are the lifetimes of $^1C^*$ and $^3C^*$, respectively, I_0 is the incident photon flux (einstein cm^{-2} s^{-1}), ε is molar extinction coefficient for ethyl cinnamate with equilibrium isomer composition, and l is the cell depth (1.0 cm). Equation (6) can be transformed to equations (7) and (8),

$$-d[C]/dt = (k_{DM}\tau_M + \Phi_{ISC}k_{DT}\tau_T)[C]\times10^3 I_0 f\times2.3\varepsilon[C] \qquad (7)$$

$$(1/[C]) - (1/[C]_0) = 2.3\times10^3 I_0\varepsilon f(\Phi'_D/[C]_0)t \qquad (8)$$

where $f=(1-10^{\varepsilon[C]_0 l})/(2.3\varepsilon[C]_0 l)$ is the correction factor for absorbed dose, and Φ'_D is the quantum yield of photodimerization at initial concentration $[C]_0$. The Φ'_D is related to the rate parameters by equation (9) for the case of degassed dilute solution.

$$\Phi'_D/[C]_0=\Phi'_{DM}/[C]_0+\Phi_{ISC}\Phi'_{DT}/[C]_0=k_{DM}\tau_M+\Phi_{ISC}k_{DT}\tau_T \qquad (9)$$

The second-order plot of reciprocal residual monomer concentration, 1/[C], against irradiation time, t, according to equation (8) was found to be linear as shown in Fig. 4, and Φ'_D was approximately calculated from the slope of this straight line.

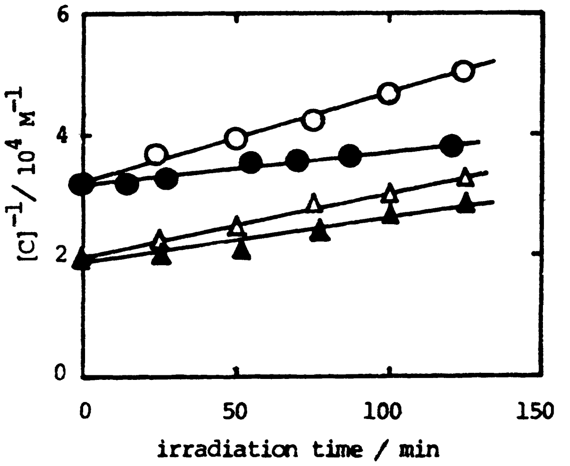

Fig. 4. Second-order plot for photodimerization of ethyl cinnamate in ethanol at 30°C.
$[C]_0$=3.10×10^{-5}M ; ○ (Vac), ● (Air)
$[C]_0$=5.10×10^{-5}M ; △ (Vac), ▲ (Air)

Oxygen has no influence on the rate of photoisomerization and the equilibrium isomer composition, but it affects photodimerization. The Φ'_D for the aerated ethanol is a half of Φ'_D for the degassed ethanol. This fact suggests that the photodimerization of ethyl cinnamate in degassed ethanol proceeds both through the excited singlet state, $^1C^*$, and through the

Table 1. Quantum yields for photodimerization of ethyl cinnamate for $[C]=[C]_0$ in ethanol irradiated at 30°C.

$[C]_0$ $(10^{-5}M)$	atmosphere	$\frac{[C_c]_e}{[C_c]_e+[C_t]_e}$	$(\Phi'_{DM}+\Phi_{ISC}\phi'_{DT})/[C]_0$ (M^{-1})	$\Phi'_{DM}/[C]_0$ (M^{-1})
2.97	Degassed	0.69	28.5	
3.10	Degassed	0.69	27.8	
3.10	Aerated	0.69		14.2
3.20	Aerated	0.70		15.4
4.29	Degassed	0.69	29.0	
5.10	Degassed	0.69	26.4	
5.10	Aerated	0.68		14.8

triplet state, $^3C^*$, as is expressed in Fig. 1. As τ_T is about 3×10^{-6} sec,11) $^3C^*$ is thoroughly quenched by oxygen in the aerated ethanol solution ($[O_2]=2.5\times10^{-3}M$,12) k_q is given by eq.(10)), and hence $\Phi'_D/[C]_0\simeq\Phi'_{DM}[C]_0=k_{DM}\tau_M$ holds for this case. The values of $(\Phi'_{DM}+\Phi_{ISC}\phi'_{DT})/[C]_0$ and $\Phi'_{DM}/[C]_0$ obtained as $\Phi'_D/[C]_0$ in degassed and aerated solutions are 28 M^{-1} and 15 M^{-1}, respectively, and are independent of $[C]_0$ as shown in Table 1. By estimating the diffusion-controlled limit for bimolecular reaction by equation (10),13)

$$k_{dif} = 8RT/3000\eta \qquad (10)$$

where η is solvent viscosity, T is temparature, and R is gas constant, we get $k_{DM} \leq 6.7\times10^9\ M^{-1}s^{-1}$, and by using it together with the above-obtained $\Phi'_{DM}/[C]_0=15\ M^{-1}$, $\tau_M \geq 2\times10^{-9}$ sec is estimated. By the subtraction of the values given in Table 1, $\Phi_{ISC}\phi'_{DT}/[C]_0 \simeq \Phi_{ISC}\tau_T k_{DT}$ is supposed to be 13 M^{-1}. Detailed discussion on the rate constants including those for photoisomerization will be given in near future.

References

1) H.G. Curme, C.C. Natale, and D.J. Kelly, J. Phys. Chem., 71, 767 (1967).
2) K. Nakamura and S. Kikuchi, Bull. Chem. Soc. Jpn., 41, 1977 (1968).
3) J. Rennert, Photogr. Sci. Eng., 15, 60 (1971).
4) G.M.J. Schmidt, Pure Appl. Chem., 27, 645 (1971).
5) M. Tsuda, Yūkigōseikagaku, 30, 589 (1972).
6) J. Rennert, S. Soloway, I. Waltcher, and B. Leong, J. Am. Chem. Soc., 94, 7242 (1972).
7) T. Ishigami, T. Murata, and T. Endo, Bull. Chem. Soc. Jpn., 49, 3578 (1976).
8) A. Reiser, P.L. Egerton, Photogr. Sci. Eng., 23, 144 (1979).
9) P.L. Egerton, E. Pitts, and A. Reiser, Macromolecules, 14, 95 (1981).
10) P.L. Egerton, E.M. Hyde, J. Trigg, A. Payne, P. Begnon, M.V. Mijovic, and A. Reiser, J. Am. Chem. Soc., 103, 3859 (1981).
11) R.B. Frings, W. Schnabel, Private communication (1980).
12) R. Fujishiro et al., "Kagaku-binran, Kisohen 2", ed by the Chem. Soc. Jpn., Maruzen, Tokyo (1975), p.775.
13) A.M. North, Quart. Rev. Chem. Soc., 20, 421 (1966).

(Received February 5, 1983)