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9,10-DICYANOANTHRACENE-SENSITIZED PHOTOISOMERIZATION OF 1,2-BIS(4-METHOXYPHENYL)CYCLOPROPANES INVOLVING A CHAIN PROCESS

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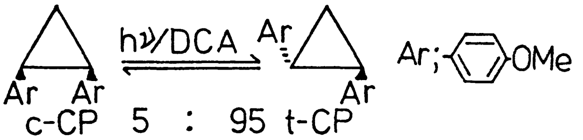
The photochemical cis-trans isomerization of cis- and trans-1,2-bis(4-methoxyphenyl)cyclopropanes sensitized by 9,10-dicyanoanthracene in aerated acetonitrile solutions proceeds via a chain process in which a cation radical produced from the cyclopropanes is involved as a chain carrier. The quantum yield for this photoisomerization is remarkably enhanced by the addition of air and phenanthrene.

The photochemical cis-trans isomerization of 1,2-diarylcyclopropanes has been extensively investigated mainly from mechanistic viewpoints.[1-3] Recently, Arnold's group[2] and Roth's group[3] have independently identified the cation radical of 1,2-diphenylcyclopropanes in CD_3CN using a photo-CIDNP method, although its chemical fate remained obscure. We now report the 9,10-dicyanoanthracene(DCA)-sensitized photoisomerization of cis- and trans-1,2-bis(4-methoxyphenyl)cyclopropanes(c-CP and t-CP) via a chain process involving a cation radical of the cyclopropanes as a chain carrier.

Irradiation of an aerated acetonitrile solution containing DCA(5×10^{-4} mol dm^{-3}) and c-CP or t-CP through an aqueous $CuSO_4$-NH_3 filter solution(405 nm light) caused the cis-trans isomerization of the cyclopropanes, ultimately affording a photostationary mixture of c-CP and t-CP in 5 : 95 ratio from both substrates(Fig. 1). At a photostationary state, the material balance was over 97%. However, the photoisomerization of cis- and trans-1,2-diphenylcyclopropanes occurred inefficiently under the similar conditions($\emptyset < 10^{-3}$).



Rates of the photoisomerization of c-CP and t-CP depended on the concentration of dissolved molecular oxygen(Fig. 1) and were remarkably enhanced by the addition of aromatic hydrocarbons such as phenanthrene(Phen) and naphthalene(Naph) in aerated acetonitrile solutions.[4]

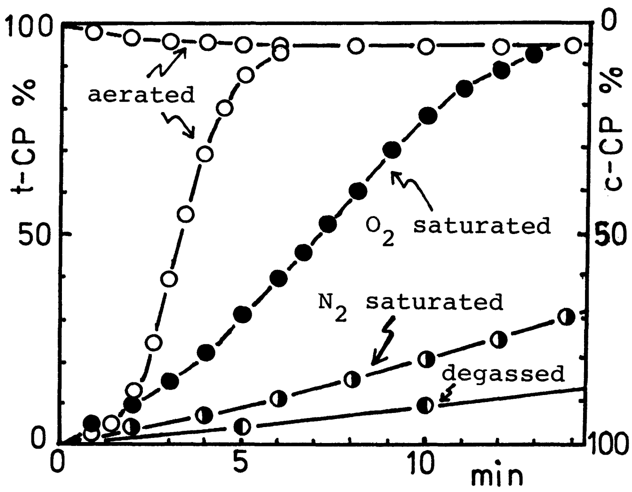


Fig. 1. Plots of c-CP and t-CP % vs. the irradiation time(min): [DCA]=5×10^{-4} mol dm^{-3}, [c-CP]=[t-CP]=1×10^{-2} mol dm^{-3} in CH_3CN at 405 nm.

Quantum yields for this photoreaction depended also on the additives and the reaction conditions(Tables 1 and 2).[5] The value of $\emptyset_{c \rightarrow t}$ exceeded largely over unity

Table 1. Effect of Molecular Oxygen on the Photoisomerization of c-CP and t-CP

Atmosphere	$\phi_{c\to t}$ a)	$\phi_{t\to c}$ a)
degassed	0.01	——
N_2 saturated	0.03	——
aerated	0.28	0.015
aerated	1.8 b)	0.1 b)
O_2 saturated c)	0.13	——

a) Values at 405 nm in CH_3CN: [DCA]=5 x 10^{-4} mol dm^{-3}, [c-CP]=[t-CP]=1 x 10^{-2} mol dm^{-3}. b) Limiting quantum yields obtained from the intercept of linear plots of 1/[ϕ] vs. 1/[CP]. c) Prolonged irradiation gave the oxygenated products of CP: Ref. 6.

Table 2. Effect of Additives on the Photoisomerization of c-CP and t-CP

Atmosphere	Additive /mol dm^{-3}	$\phi_{c\to t}$ a)	$\phi_{t\to c}$ a)
aerated	none	0.28	0.015
	Phen 1 x 10^{-2}	13.0	0.70
	Phen 1 x 10^{-1}	13.4	——
	Naph 1 x 10^{-2}	12.5	——
	DABCO 5 x 10^{-3}	0	0
	TEA 5 x 10^{-3}	0	0
degassed	none	0.01	——
	Phen 1 x 10^{-2}	2.8	——

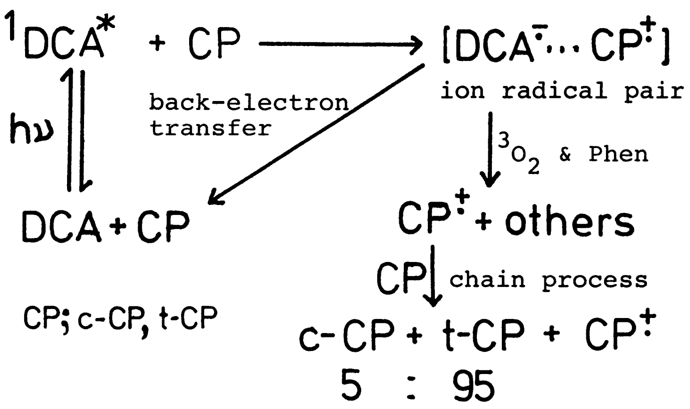
a) Values at 405 nm in CH_3CN: [DCA]=5 x 10^{-4} mol dm^{-3}, [c-CP]=[t-CP]=1 x 10^{-2} mol dm^{-3}.

in the presence of air and aromatic hydrocarbons. The photoisomerization was completely quenched by the addition of 1,4-diazabicyclo[2.2.2]octane(DABCO) or triethylamine(TEA). The fluorescence of DCA in acetonitrile was quenched by c-CP, t-CP, Phen, Naph, DABCO, and TEA in near diffusion controlled rates.6)

The photoisomerization of c-CP and t-CP occurred inefficiently($\phi < 0.01$) in less polar solvents such as dichloromethane, ethyl acetate, and benzene although the fluorescence of DCA was quenched efficiently in these solvents.

A proposed mechanism for the photoisomerization is shown in Scheme 1. A cation radical($CP^{\dot{+}}$) produced via an electron transfer from the cyclopropanes to the excited DCA promotes a chain process through a hole transfer from $CP^{\dot{+}}$ to CP. The enhancement of the quantum yields by the addition of air and aromatic hydrocarbons is most probably ascribed to the suppression of the back-electron transfer from $DCA^{\dot{-}}$ to $CP^{\dot{+}}$.7)

Scheme 1.



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2) P. C. Wong and D. R. Arnold, Tetrahedron Lett., 20, 2101(1979) and references therein.
3) H. D. Roth and M. L. M. Schilling, J. Am. Chem. Soc., 102, 7956(1980).
4) The photo-retrocycloaddition of dimethylthymine dimers in the presence of an electron acceptor has been found to be accelerated by O_2 and aromatic hydrocarbons: T. Majima, C. Pac, J. Kubo, and H. Sakurai, Tetrahedron Lett., 21, 377(1980); C. Pac, J. Kubo, T. Majima, and H. Sakurai, Photochem. Photobiol., 36, 273(1982).
5) The quantum yields for the photoisomerization in the presence of O_2 were estimated from the slopes of the linear parts of plots in the region of 30-70% conversions in Fig. 1.
6) K. Mizuno, N. Kamiyama, and Y. Otsuji, Chem. Lett., 1983, 477.
7) For the suppression of the back-electron transfer, several processes could be considered: For example, $[DCA^{\dot{-}}\cdots CP^{\dot{+}}] + {}^3O_2 \rightarrow DCA + O_2^{\dot{-}} + CP^{\dot{+}}$, $[DCA^{\dot{-}}\cdots CP^{\dot{+}}]$ + Phen $\rightarrow DCA^{\dot{-}} + [CP\cdots Phen]^{\dot{+}}$: Cf. J. Eriksen and C. S. Foote, J. Am. Chem. Soc., 102, 6083(1980); D. S. Steichen and C. S. Foote, ibid., 103, 1855(1981); T. Majima, C. Pac, A. Nakasone, and H. Sakurai, ibid., 103, 4499(1981), and references therein.

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