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CIS-TRANS PHOTOISOMERIZATION AND PHOTOOXYGENATION OF 1,2-DIARYLCYCLOPROPANES. SALT EFFECTS ON THE PHOTOINDUCED ELECTRON TRANSFER REACTIONS

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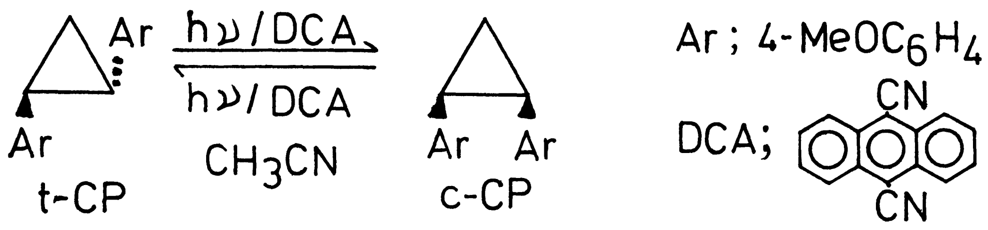
The efficiencies of the 9,10-dicyanoanthracene (DCA)-sensitized cis-trans photoisomerization and photooxygenation of cis- and trans-1,2-bis(4-methoxyphenyl)cyclopropanes (c-CP and t-CP) in CH_3CN were remarkably enhanced by the addition of inorganic salts such as $LiBF_4$ and $Mg(ClO_4)_2$. The mechanistic implication of the salt effects on these photoreactions was discussed.

Photoinduced electron transfer reactions between electron donor (D) and electron acceptor (A) in polar media have been the subject of considerable interest from the mechanistic and synthetic viewpoints.[1] In these photoreactions, the separation of initially produced radical ion-pair ($[A^{\bullet -}\cdots D^{\bullet +}]$) into dissociated radical ions $A^{\bullet -}$ and $D^{\bullet +}$ is crucial in determining the efficiency of the photoreactions. We have envisioned that this separation may be facilitated by the addition of some additives in modes of Scheme 1, where X and Y are the additives that can stabilize $A^{\bullet -}$ and $D^{\bullet +}$ by interaction with the respective radical ions. Recently, we have reported that molecular dioxygen and aromatic hydrocarbons act as X and Y respectively and thereby enhance the quantum efficiency of the photoisomerization of 1,2-diarylcyclopropanes.[2] There is also the possibility that in a certain metal salt, metal cation serves as X and its gegen anion as Y.[3] From this point of view, we have studied the effect of metal salt on the cis-trans photoisomerization and photooxygenation of cis- and trans-1,2-bis(4-methoxyphenyl)-cyclopropanes (c-CP and t-CP) that proceed via photoinduced electron transfer.

$$
\begin{array}{l}
A^{*} + D \ \text{or}\ A + D^{*} \rightleftharpoons [A^{\bullet -}\cdots D^{\bullet +}] \rightleftharpoons A^{\bullet -} + D^{\bullet +} \\
[A^{\bullet -}\cdots D^{\bullet +}] + X \longrightarrow [A\cdots X]^{\bullet -} + D^{\bullet +} \\
[A^{\bullet -}\cdots D^{\bullet +}] + Y \longrightarrow A^{\bullet -} + [D\cdots Y]^{\bullet +} \\
[A^{\bullet -}\cdots D^{\bullet +}] + X + Y \longrightarrow [A\cdots X]^{\bullet -} + [D\cdots Y]^{\bullet +}
\end{array}
$$

Scheme 1.

9,10-Dicyanoanthracene (DCA)-sensitized photoisomerization of either c-CP or t-CP in CH_3CN affords the same photostationary state which contains c-CP and t-CP in a 5 : 95 ratio.[2,4] The quantum efficiency of this photoisomerization was remarkably enhanced upon the addition of $LiBF_4$ or $Mg(ClO_4)_2$, while the photostationary state was the same as that in the absence of the salts. The rates of the photoisomerization of c-CP and t-CP in the absence of the salts depended on the concentration of dissolved oxygen.$^{2)}$ However, the quantum yield for the



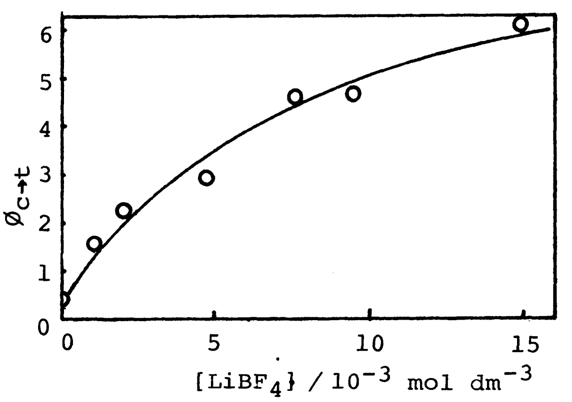


Fig. 1. Plot of quantum yield ($\phi_{c\rightarrow t}$) vs. the concentration of $LiBF_4$ in aerated acetonitrile solution: 405 nm irradiation; [DCA]=5 x 10^{-4}mol/dm^3, [c-CP]=1 x 10^{-2}mol/dm^3.

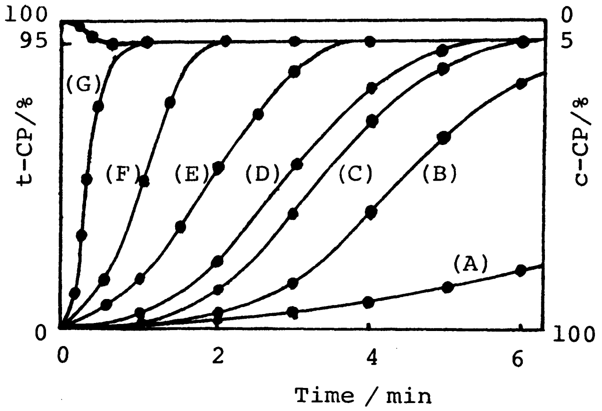


Fig. 2. Plots of c-CP and t-CP % vs. the irradiation time (min) in the presence of metal salts in aerated acetonitrile solutions; [DCA]=5 x 10^{-4}mol/dm^3, [CP]= 1 x 10^{-2}mol/dm^3, $[M^+X^-]$=5 x 10^{-3}mol/dm^3. For (A) - (G) ; see Table 1.

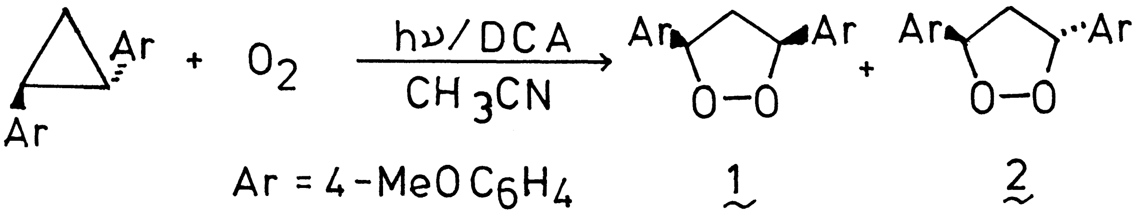
Table 1. Effect of Metal Salts on the Photoisomerization of c-CP to t-CP$^{a)}$

Additive		mol/dm^3	$\phi_{c\rightarrow t}$$^{b)}$	$\phi_{c\rightarrow t}$$^{c)}$
(A)	none		0.28$^{d)}$	0.01$^{d)}$
(B)	$KClO_4$	5.0 x 10^{-3}	2.3	——
(C)	$LiBF_4$	5.0 x 10^{-3}	2.9	——
	$LiBF_4$	1.0 x 10^{-2}	4.7	4.2
(D)	Et_4NClO_4	5.0 x 10^{-3}	3.3	——
(E)	$NaClO_4$	5.0 x 10^{-3}	3.8	——
(F)	$LiClO_4$	5.0 x 10^{-3}	5.4	——
(G)	$Mg(ClO_4)_2$	2.5 x 10^{-3}	10.9	——

a) Values at 405 nm in CH_3CN: [DCA]=5 x 10^{-4}mol/dm^3, [c-CP]=1 x 10^{-2}mol/dm^3 : Ref. 5. b) Aerated solution. c) Degassed solution. d) Values from Ref. 2.

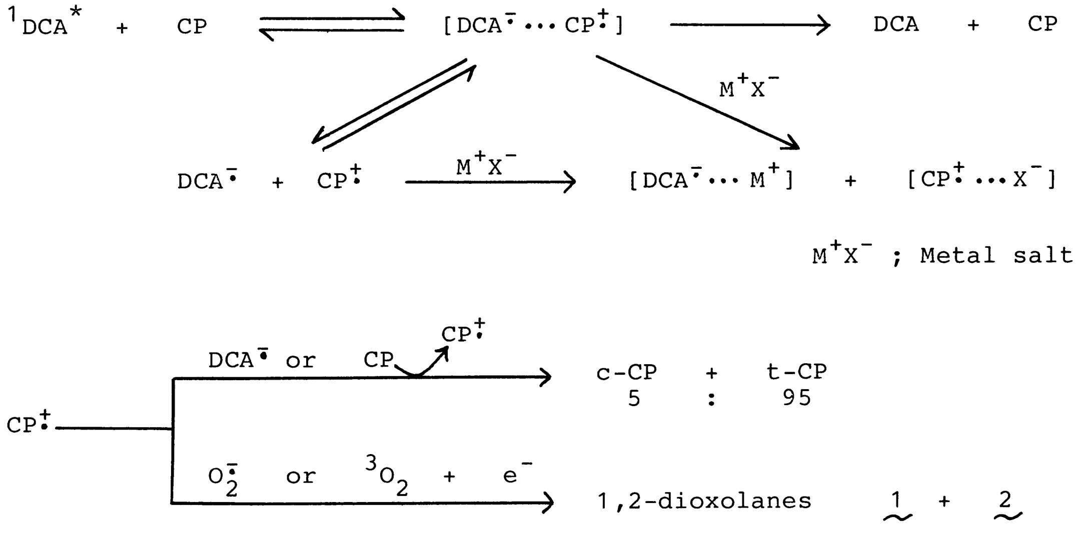
photoisomerization ($\Phi_{c\rightarrow t}$) in the presence of $LiBF_4$ remained at the almost same values both in degassed and aerated solutions (Table 1),[2,5] and it depended on the concentration of the dissolved salt (Fig. 1). The effects of other salts were also examined. The results were summarized in Table 1 and Fig. 2. In general, the induction period which depended on the nature of the added salts were observed in this photoreaction. The addition of LiCl or LiBr (0.001 mol dm^{-3}) into the reaction system completely quenched the photoisomerization.

Irradiation of a CH_3CN solution containing DCA (0.2 mmol) and t-CP (4 mmol) under a continuous oxygen stream in the presence of $LiBF_4$ (2 mmol) for 10-20 min afforded cis- and trans-3,5-bis(4-methoxyphenyl)-1,2-dioxolanes (1 and 2) in > 90% yields.[6] The photoreaction in the presence of $LiClO_4$ and $Mg(ClO_4)_2$ yielded the same products in excellent yields. The DCA-sensitized photooxygenation of trans-1-phenyl-2-(4-methoxyphenyl)cyclopropane and trans-1-(4-chlorophenyl)-2-(4-methoxyphenyl)cyclopropane proceeded also smoothly in the presence of these metal salts. The rates of the photooxygenation in the presence of these salt were 5-10 times faster than that in the absence of the metal salts although the product ratio of 1 to 2 (7 : 3) remained unchanged.



The fluorescence of DCA in CH_3CN was efficiently quenched by c-CP and t-CP at nearly diffusion controlled rates. The free energy change (ΔG) for the electron transfer process from CP to the excited singlet DCA ($^1DCA^*$) was estimated to be negative.[2,6] However, the fluorescence of DCA in CH_3CN was not quenched by $LiBF_4$ or $Mg(ClO_4)_2$. The rate constant of fluorescence quenching by t-CP was not affected by $LiBF_4$ or $Mg(ClO_4)_2$. The quantum yields for the photoisomerization, $\Phi_{c\rightarrow t}$, exceeded largely over unity in the presence of these salts (Table 1).

All the above results may be explained in terms of the mechanism shown in Scheme 2. The first step is one-electron transfer from CP to $^1DCA^*$ to form the radical ion pair [$DCA^{\overset{-}{\cdot}}$···$CP^{\overset{+}{\cdot}}$]. The dissociation of the radical ion pair to the free radical ions competes with back-electron transfer from $DCA^{\overset{-}{\cdot}}$ to $CP^{\overset{+}{\cdot}}$. The free radical cation $CP^{\overset{+}{\cdot}}$ undergoes the cis-trans isomerization and also induces a chain process in this isomerization through the electron transfer from CP to $CP^{\overset{+}{\cdot}}$. The reaction of $CP^{\overset{+}{\cdot}}$ with molecular dioxygen ($^3O_2$) or with $O_2^{\overset{-}{\cdot}}$ which is generated by the electron transfer from $DCA^{\overset{-}{\cdot}}$ to $^3O_2$ gives the radical cations of the dioxolanes or the dioxolanes themselves.[7] The electron transfer from CP or $DCA^{\overset{-}{\cdot}}$ to the dioxolane radical cations affords also 1 and 2.[6] The enhancement of the quantum efficiencies in the above photoreaction by the addition of metal salts suggests that the back-electron transfer from $DCA^{\overset{-}{\cdot}}$ to $CP^{\overset{+}{\cdot}}$ is perhaps suppressed through ionic interaction of the radical ion species with the added metal salts.



Scheme 2.

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4) Irradiation was carried out through a Toshiba KL-40 glass filter and an aqueous NH_3-$CuSO_4$ filter solution (405 nm light) using a 500 W high-pressure mercury lamp.

5) The quantum yields for the photoisomerization in the presence of the metal salts were estimated from the slopes of linear parts of the plots in the region of 30-70% conversions in Fig. 2.

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