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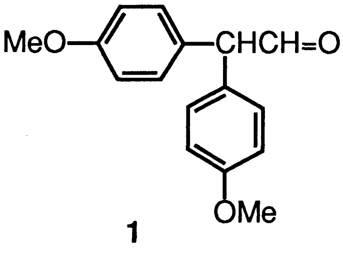
Photoinduced Electron Transfer Reactions of Di(4-methoxyphenyl)ethanal in Solution. Sensitizer-dependent Decay Pathways of the Aldehyde Cation Radical

Ryoichi AKABA,†* Masaki KAMATA,†† Yasunao KURIYAMA,††† Hirochika SAKURAGI,†††*
and Katsumi TOKUMARU†††
† Department of Chemistry, Gunma College of Technology, Toriba-machi, Maebashi, Gunma 371
†† Department of Chemistry, Niigata University, Ikarashi, Niigata, Niigata 950-21
††† Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

Laser flash photolyses of di(4-methoxyphenyl)ethanal in the presence of electron-accepting sensitizers such as 2,4,6-triphenylpyrylium tetrafluoroborate and 9,10-dicyanoanthracene have been carried out. Chemical properties of the sensitizers or their one-electron reduced species and an added electrolyte greatly influenced the reaction course of the photogenerated aldehyde cation radical in solution.

Although chemistry of cation radicals generated from photoinduced electron transfer (PET) in solution has gathered increasing attention,1) laser flash photolysis (LFP) studies of cation radicals with oxygen functional groups such as those of ketones and aldehydes have only recently been reported.2) LFP is one of the most powerful tools to elucidate the diverse reactivity of the reactive intermediates generated by PET;3) however, there have been few LFP approaches which have revealed sensitizer-dependent reactivities of cation radicals in solution.

We wish to report here that di(4-methoxyphenyl)ethanal cation radical $\mathbf{1}^{+\cdot}$ generated from PET of the parent aldehyde **1** has two predominant decay pathways depending on the sensitizers employed. The results show that 2,4,6-triphenylpyrylium ($TPP^+BF_4^-$) and 2,4,6-triphenylthiapyrylium tetrafluoroborate ($STPP^+BF_4^-$) as sensitizers favor the C-C bond cleavage of $\mathbf{1}^{+\cdot}$ to afford a di(4-methoxyphenyl)methyl cation **2** and a formyl radical, whereas such C-C bond cleavage cannot be observed when 9,10-dicyanoanthracene (DCA) is employed as a sensitizer. Furthermore, addition of $LiBF_4$ again favors the C-C bond cleavage in the DCA-sensitized reactions. The present work is the first LFP approach that offers clear evidence that an aldehyde cation radical behaves differently depending on the sensitizers employed.



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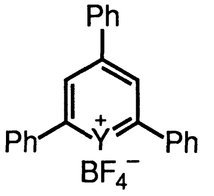
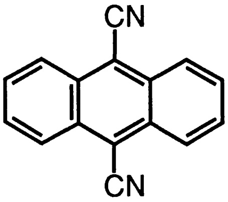


Y = O: $TPP^+BF_4^-$
Y = S: $STPP^+BF_4^-$



DCA

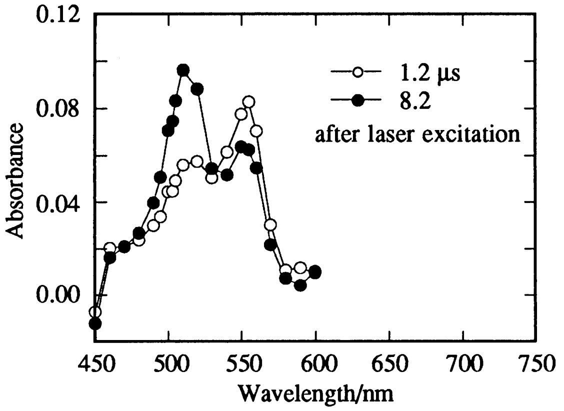


Fig. 1. Transient spectra obtained by laser excitation of $TPP^+BF_4^-$ (6.5×10^{-5} M) in the presence of **1** (2.1×10^{-3} M) in CH_2Cl_2 under argon.

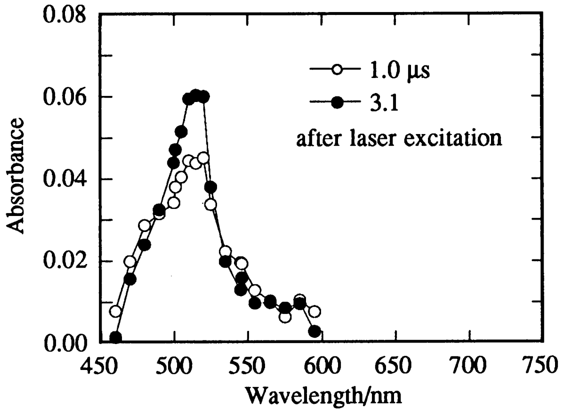


Fig. 2. Transient spectra obtained by laser excitation of $STPP^+BF_4^-$ (5.3×10^{-5} M) in the presence of **1** (2.1×10^{-3} M) in CH_2Cl_2 under argon.

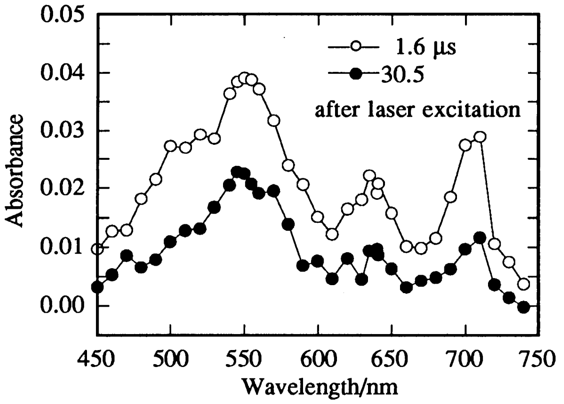


Fig. 3. Transient spectra obtained by laser excitation of DCA ($\approx10^{-4}$ M) in the presence of **1** (1.9×10^{-2} M) in CH_3CN under argon.

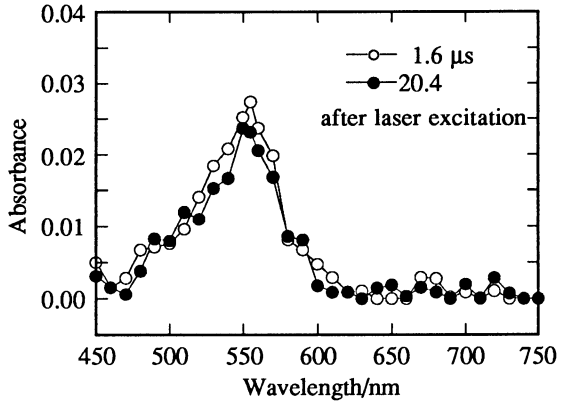


Fig. 4. Transient spectra obtained by laser excitation of DCA ($\approx10^{-4}$ M) in the presence of **1** (1.9×10^{-2} M) in CH_3CN under oxygen.

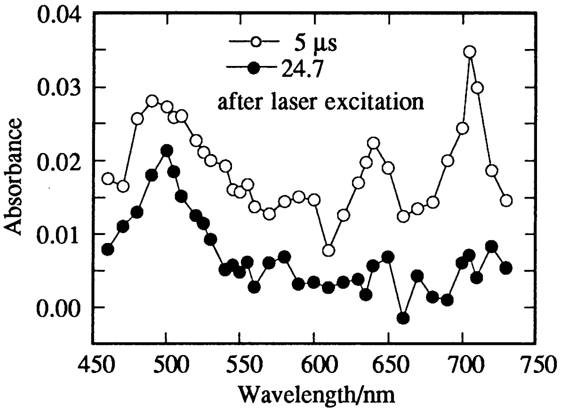
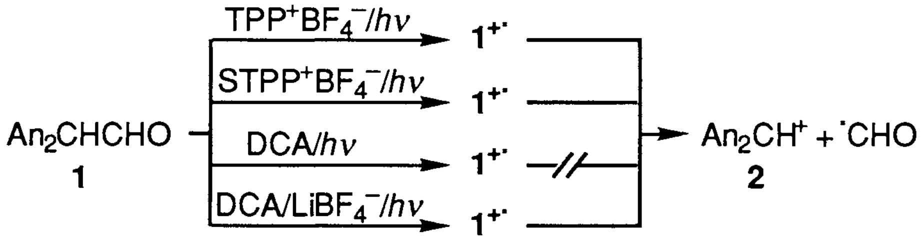


Fig. 5. Transient spectra obtained by laser excitation of DCA (2.2×10^{-4} M) in the presence of **1** (2.0×10^{-2} M) and $LiBF_4$ (0.11 M) in CH_3CN under argon.

Typically, LFP of $TPP^+BF_4^-$ (6.5×10^{-5} M, M=mol dm^{-3}) in the presence of **1** (2.1×10^{-3} M) in CH_2Cl_2 with an excimer laser-pumped dye laser (408 nm) under argon gave transient spectra shown in Fig. 1.4,5) The 510- and 550-nm bands were assigned to **2**6) and a superposition of $\mathbf{1}^{+\cdot}$7) and pyryl radicals (TPP·),3a) respectively. The fact that the 550-nm band starts to decay while the 510-nm band increases in intensity is consistent with the formation of **2** with concomitant decomposition of $\mathbf{1}^{+\cdot}$ though the rates for the decay at 550 nm and the rise at 510 nm are not identical because of slow consumption of TPP·. In order to confirm the above assignment, LFP of **1** was also carried out with $STPP^+BF_4^-$ as a sensitizer under similar conditions, since the one-electron reduced species of $STPP^+$, a thiapyryl radical (STPP·), has no absorption in this region (550 nm).[8] Thus, LFP of $STPP^+BF_4^-$ (5.3×10^{-5} M) in the presence of **1** (2.1×10^{-3} M) in CH_2Cl_2 gave a transient spectrum assignable to **2** at 510 nm (Fig. 2).

In contrast with the $TPP^+BF_4^-$- or $STPP^+BF_4^-$-sensitized reactions, LFP of **1** with DCA gave quite different transient behavior of $\mathbf{1}^{+\cdot}$. When LFP of DCA ($\approx 10^{-4}$ M) in the presence of **1** (1.9×10^{-2} M) was carried out in CH_3CN under argon (425 nm excitation), transient spectra shown in Fig. 3 were obtained. Figure 3 shows that a relatively large absorption band at 550 nm is observed in addition to a group of bands at 510, 640, and 710 nm, which are assigned to the anion radical of DCA ($DCA^{-\cdot}$) on the basis of the reported spectrum[9] and their disappearance in the presence of oxygen. LFP of **1** with DCA in the presence of oxygen exhibited transient spectra (Fig. 4) where only the 550-nm band remained, and all the other bands assignable to $DCA^{-\cdot}$ disappeared due to rapid electron transfer from $DCA^{-\cdot}$ to molecular oxygen.[10] The 550-nm band can be attributed to $\mathbf{1}^{+\cdot}$ on the basis of the above results, its formation in the early stage on laser excitation and the low reactivity with molecular oxygen.

These results indicate that the C-C bond cleavage of $\mathbf{1}^{+\cdot}$ does not occur in the DCA sensitization of **1**. The 550-nm band was replaced by a 500-nm band when LFP of **1** (2.0×10^{-2} M) with DCA (2.2×10^{-4} M) was carried out in the presence of $LiBF_4$ (0.11 M) in CH_3CN under argon, as shown in Fig. 5 . The 500-nm band at a later stage of transient spectra is attributed to the carbocation **2**.[11,12] The results suggest that nucleophilicity of BF_4^- plays an important role in effecting the C-C bond cleavage of $\mathbf{1}^{+\cdot}$.[13,14]



Scheme 1.

In conclusion, the present observations may be summarized in Scheme 1. We have offered LFP evidence that the reaction mode of the aldehyde cation radical generated from PET is greatly influenced by the chemical properties of the one-electron reduced species of sensitizers and/or the added electrolyte corresponding the counter ions of sensitizers. The results suggest that $\mathbf{1}^{+\cdot}$ undergoes deprotonation or hydrogen atom transfer when it constitutes an radical ion pair with a DCA anion radical in CH_3CN while it predominantly undergoes the C-C bond cleavage to afford **2** when TPP·, STPP·, or BF_4^- exists in the proximity of $\mathbf{1}^{+\cdot}$ in CH_2Cl_2. The addition of $LiBF_4$ can inhibit the competing reaction which otherwise occurs in DCA-sensitized reactions in CH_3CN, and it consequently favors the C-C bond cleavage as is the cases for $TPP^+BF_4^-$- and $STPP^+BF_4^-$-sensitized reactions in CH_2Cl_2. Further studies to examine the scope and generality of the sensitizer-dependent reactivity of cation radicals as well as the product studies for **1** are in progress.

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