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# $S_N$1-Type Mechanism for the Carbon-Carbon Bond Cleavage of Tetrakis(4-methylphenyl)ethanone Cation Radical. A Laser Flash Photolysis Study

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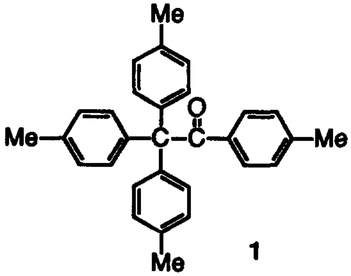
***Abstracts:*** *On the basis of measurements of rate constants for carbon-carbon bond cleavage of tetrakis(4-methylphenyl)ethanone cation radicals generated by pulsed laser excitation with sensitizers in solution, an $S_N$1-type mechanism for the bond cleavage is proposed.*

Although much attention has been directed toward the chemistry of cation radicals generated from photoinduced electron transfer (PET),[1,2] laser flash photolysis (LFP) studies on the C-C bond cleavage of cation radicals have only recently been reported.[3] We have recently shown that a tetrakis(4-methylphenyl)ethanone cation radical $1^{+\cdot}$ undergoes carbon-carbon bond cleavage in $CH_2Cl_2$ to afford a tris(4-methylphenyl)methyl cation **2** and a 4-methylbenzoyl radical.[3] The reaction may be regarded as a photosolvolytic reaction through the cation radicals with a 4-methylbenzoyl group as a leaving group. The photosolvolysis via cation radicals may be an interesting counterpart of the long-known photosolvolysis of charged or neutral molecules (Reactions 1 and 2).[4]

$$\text{R-E} \xrightarrow{h\nu} \text{R}^+ + \text{E}^- \qquad (1)$$

$$\text{R-E} \xrightarrow{h\nu/\text{Sensitizer}} \text{R-E}^{+\cdot} \longrightarrow \text{R}^+ + \text{E}^\cdot \qquad (2)$$



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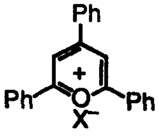
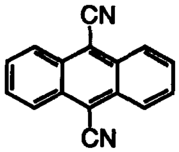


TPP⁺X⁻



DCA

We point out here that the C-C bond cleavage of $1^{+\cdot}$ generated by PET in solution proceeds through an $S_N$ 1-type mechanism with a distinct carbocation intermediate (**2**). The present work is an LFP approach on the C-C bond cleavage of $1^{+\cdot}$ with changing the sensitizers, solvents, and reaction atmospheres. Transient absorption spectra were recorded under a variety of conditions, and the rate constants for C-C bond cleavage in $1^{+\cdot}$, as measured by the build-up of **2**, are summarized in Table 1. Carbocation **2** could be observed in all the cases shown in Table 1 (vide infra).

Typically, when a $CH_2Cl_2$ solution of $TPP^+ClO_4^-$ ($6.5\times10^{-5}$ M) in the presence of **1** ($2.8\times10^{-2}$ M) was irradiated under argon with an excimer laser-pumped dye laser (408-nm excitation), transient spectra (not shown) were obtained, indicating the formation of **2** (455 nm)[5] and pyryl radicals (550 nm).[3a] The kinetic analysis of the 455-nm band gave the C-C bond cleavage rate constant for $1^{+\cdot}$ to be $1.6\times10^7$ $M^{-1}$ $s^{-1}$. Neither effects of the counter ions ($X^-$) nor effect of oxygen (in the case of $BF_4^-$ salt) were observed on the rate constant (Table 1). In view of a possible nucleophilic assistance of MeOH in the C-C bond cleavage of $1^{+\cdot}$, LFP of **1** in the presence of MeOH was also carried out. LFP of $TPP^+BF_4^-$ ($6.2\times10^{-5}$ M) in the presence of **1** ($2.8\times10^{-2}$ M) in $CH_2Cl_2$/MeOH (4:1 in v/v) gave transient spectra shown in Figure 1. Figure 1 indicates the formation of 455 nm and TPP· (550 nm) bands, showing that **2** is also formed as a distinct intermediate in the presence of MeOH. The observed first-order rate constant for build-up of the 455-nm band ($8.3\times10^6$ $s^{-1}$) in Figure 1 is similar to that observed in $CH_2Cl_2$, which is consistent with the clear observation of **2** in both cases.

9,10-Dicyanoanthracene (DCA) was also employed to see whether this cyanoaromatic sensitizer may actually generate $1^{+\cdot}$ which further undergoes the C-C bond cleavage to afford **2** in $CH_3CN$.[6] When DCA ($2.8\times10^{-4}$ M) was irradiated with an excimer laser-pumped dye laser (425 nm) in the presence of **1** ($3.0\times10^{-2}$ M) under argon atmosphere, a transient spectrum (not shown)

Table 1. First-Order Rate Constants for the C-C bond Cleavage of $1^{+\cdot}$ [a]

| Run | Sensitizer | Solvent | Atmosphere | $k$/$s^{-1}$ |
|---|---|---|---|---|
| 1 | $TPP^+BF_4^-$ | $CH_2Cl_2$ | Ar | $1.5\times10^7$ |
| 2 | $TPP^+BF_4^-$ | $CH_2Cl_2$ | $O_2$ | $1.4\times10^7$ |
| 3 | $TPP^+BF_4^-$ | $CH_2Cl_2$/MeOH | Ar | $8.3\times10^6$ |
| 4 | $TPP^+ClO_4^-$ | $CH_2Cl_2$ | Ar | $1.6\times10^7$ |
| 5 | $TPP^+PF_6^-$ | $CH_2Cl_2$ | Ar | $1.0\times10^7$ |
| 6 | DCA | $CH_3CN$ | Ar | $\sim6\times10^6$ [b] |
| 7 | DCA | $CH_3CN$ | $O_2$ | $1.0\times10^7$ |

a) Measured at ambient temperature (ca. 25 °C). b) The uncertainty of this rate constant might be larger because the strong fluorescence of $^1DCA^*$ disturbed to some degree the build-up curve of cation.

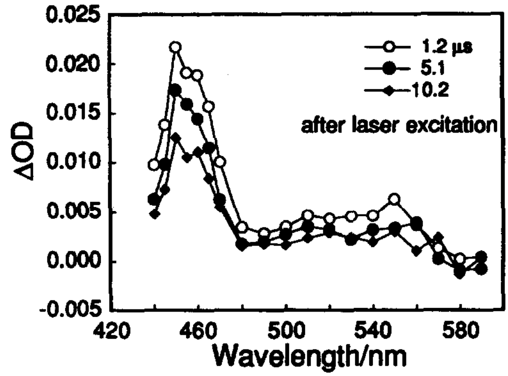


Figure 1. Transient absorption spectra of $TPP^+BF_4^-$ ($6.2 \times 10^{-5}$ M) in the presence of 1 ($2.8 \times 10^{-2}$ M) in $CH_2Cl_2$/MeOH (4:1 in v/v) under argon.

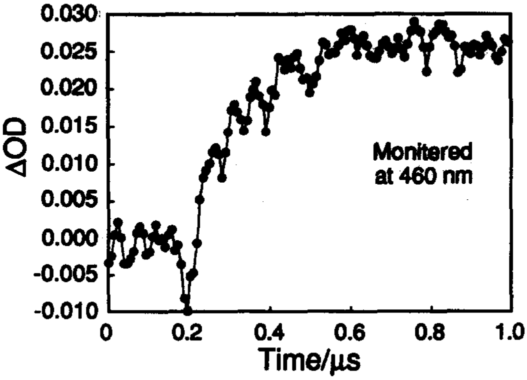


Figure 2. A kinetic profile of the 455-nm band. For conditions, see the captions of Figure 1.

was obtained, showing the formation of 2 and DCA anion radicals ($DCA^{-\cdot}$); the assignment of the latter is secured on the basis of the reported spectrum.[7] Time dependence of the transient spectra is nicely consistent with the initial electron transfer from 1 to the excited singlet state of DCA ($^1DCA^*$), giving $1^{+\cdot}$ and $DCA^{-\cdot}$, the resulting $1^{+\cdot}$ undergoing the C-C bond cleavage to afford 2. Carbocation 2 was also formed in the presence of oxygen though the absorption assignable to $DCA^{-\cdot}$ disappeared through a rapid electron transfer from $DCA^{-\cdot}$ to molecular oxygen.[5,8] The rate constant for C-C bond cleavage of $1^{+\cdot}$ in $CH_3CN$ in the presence of oxygen is $1.0 \times 10^7$ $s^{-1}$,[9] which is similar to that observed in $TPP^+$-sensitized reactions in $CH_2Cl_2$.

All these facts as well as the observation of 2 in all the cases studied are consistent with a mechanism involving a distinct carbocation intermediate formed by a spontaneous C-C bond cleavage in $1^{+\cdot}$ without significant assistance of solvent and counter ions ($X^-$). It is noted that the addition of methanol, a good nucleophilic solvent which may attack a developing cationic center and/ or solvate cationic intermediates like 2, did not increase the cleavage rate constant at all. This is in contrast with the results that a C-Si bond cleavage of photogenerated benzyltrimethylsilane radical cations is accelerated by addition of MeOH in $CH_3CN$,[3d,e]; the results are attributed to the nucleophilic assistance of methanol to effect the C-Si bond cleavage.

In conclusion, we have shown that the substituted benzoyl group in 1 can be an extremely good leaving group to generate carbocation 2 if the substrate is activated to its cation radical via PET. A driving force for the $S_N$-1 type mechanism in the bond cleavage may be the formation of the resonance-stabilized carbocation 2. The present work has also revealed a new decay pathway for carbocation 2 which may react with $O_2^{-\cdot}$. This cannot occur in the $TPP^+$-sensitized electron transfer oxygenation where the superoxide is not formed in the medium.[10] Further studies on the photosolvolysis via cation radicals are underway on substrates with other potential leaving groups as well as on the product studies of the present system.

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6 LFP experiments with TPP$^+$ $BF_4^-$ in $CH_3CN$ were unsuccessful because of rapid bleaching of the sensitizer in this solvent. Further works are underway.

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9 Strong fluorescence from DCA obscured to some degree at the early stage of the build-up of the absorption band. This is not crucial in the experiments in the presence of oxygen.

10 Actually, the decay profile of **2** in the presence of oxygen could be analyzed well by the second-order kinetics ($k/\varepsilon = 2.2 \times 10^6$ cm s$^{-1}$), being consistent with its decay by the reaction with $O_2^{-\bullet}$.

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