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S_N1-Type Mechanism for the Carbon-Carbon Bond Cleavage of Tetrakis(4-methylphenyl)ethanone Cation Radical. A Laser Flash Photolysis Study

Ryoichi Akaba,[a,*] Masaki Kamata,[b] Hirochika Sakuragi,[c] and Katsumi Tokumaru[c]

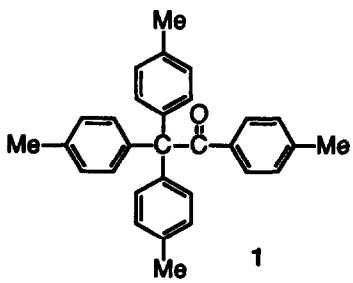
[a] Department of Chemistry, Gunma College of Technology, Toriba-machi, Maebashi, Gunma 371, Japan, [b] Department of Chemistry, Faculty of Education, Niigata University, Ikarashi, Niigata 950-21, Japan, and [c] Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

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_N1-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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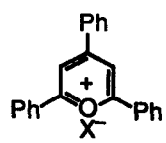
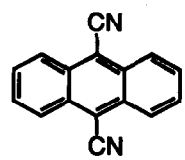


TPP⁺X⁻



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 $TPP^+ClO_4^-$ (6.5×10^{-5} M) in the presence of **1** (2.8×10^{-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 1.6×10^7 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 $TPP^+BF_4^-$ (6.2×10^{-5} M) in the presence of **1** (2.8×10^{-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 $TPP\cdot$ (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 (8.3×10^6 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 (2.8×10^{-4} M) was irradiated with an excimer laser-pumped dye laser (425 nm) in the presence of **1** (3.0×10^{-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	1.5×10^7
2	$TPP^+BF_4^-$	CH_2Cl_2	O_2	1.4×10^7
3	$TPP^+BF_4^-$	CH_2Cl_2/MeOH	Ar	8.3×10^6
4	$TPP^+ClO_4^-$	CH_2Cl_2	Ar	1.6×10^7
5	$TPP^+PF_6^-$	CH_2Cl_2	Ar	1.0×10^7
6	DCA	CH_3CN	Ar	$\sim6\times10^6$ [b]
7	DCA	CH_3CN	O_2	1.0×10^7

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.

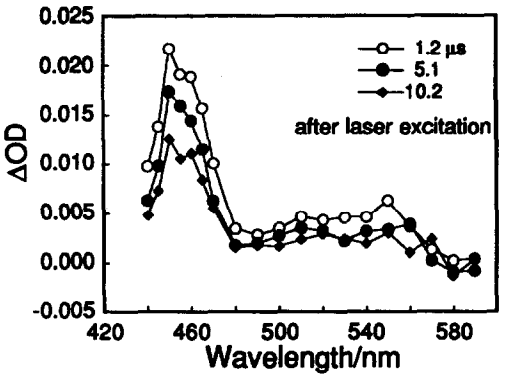


Figure 1. Transient absorption spectra of $TPP^+BF_4^-$ (6.2×10^{-5} M) in the presence of **1** (2.8×10^{-2} M) in CH_2Cl_2/MeOH (4:1 in v/v) under argon.

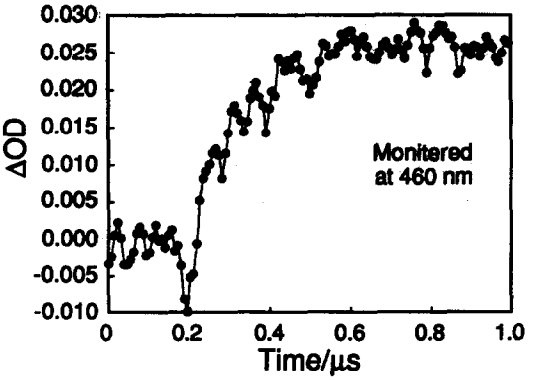


Figure 2. A kinetic profile of the 455-nm band. For conditions, see the captions of Figure 1.

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 $\mathbf{1}^{+\cdot}$ and $DCA^{-\cdot}$, the resulting $\mathbf{1}^{+\cdot}$ 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 $\mathbf{1}^{+\cdot}$ in CH_3CN in the presence of oxygen is 1.0×10^7 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 $\mathbf{1}^{+\cdot}$ 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_N1 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 $O_2^{-\cdot}$.

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