Bull. Chem. Soc. Jpn., 68, 277—281(1995)

Attempts at Direct Detection of Reactive Species in Selective Excitation of the Contact Charge Transfer Pairs of Hexamethylbenzene and Oxygen

Toshiki Komatsu, Masahiro Tsuchiya, Gen-ichi Furusawa, Yasunao Kuriyama,
Hirochika Sakuragi,* Fusae Nakanishi,† and Katsumi Tokumaru*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305
†Joint Graduate School of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

(Received July 8, 1994)

Pulsed laser excitation of contact charge transfer pairs of hexamethylbenzene (HMB) and oxygen in methanol–acetonitrile gave no evidence for intermediacy of reactive species such as HMB radical cations and pentamethylbenzyl cations ($ArCH_2^+$), though stationary irradiation of the pair in hydroxylic solvents afforded distinct products arising from the cationic species. The mechanism of reactions was discussed in comparison with 9,10-dicyanoanthracene-sensitized oxygenation of HMB.

Many organic compounds have been known to interact with molecular oxygen in the ground state, leading to the reversible formation of contact charge transfer (CCT) pairs.[1] We have been interested in characteristic photochemical reactions resulting from selective excitation of CCT pairs in solution,[2] and revealed that the excitation of CCT pairs of hexamethylbenzene (HMB) and oxygen in benzene–methanol or acetonitrile–methanol with 313-nm light gave methoxymethylpentamethylbenzene ($C_6Me_5CH_2OMe$, **1a**) as a main product. We attributed the formation of **1a** to intervention of pentamethylbenzyl cations ($C_6Me_5CH_2^+$) produced from the HMB radical cations ($HMB^{+\bullet}$).[2a,2b] This reaction is contrasted to those observed on direct excitation of HMB under oxygen with 254-nm light[2a] and on dye-sensitized irradiation of HMB under oxygen with visible light,[3,4] since the former leads to autoxidation of the methyl groups to afford 3,4,5,6-tetramethylphthalide (**2**) and the latter to production of singlet oxygen to yield a hydroperoxy-endoperoxide. 9,10-Dicyanoanthracene (DCA)-sensitized irradiation of HMB under aerated conditions also exerted a different feature. Various polymethylbenzenes form CCT pairs with oxygen as shown by their absorptions; however, only HMB gives the methoxylated product on irradiation in a mixture of methanol and acetonitrile or benzene.[2a] Under similar conditions, 1,2,4,5-tetramethylbenzene (durene), 1,3,5-trimethylbenzene (mesitylene), 1,4-dimethylbenzene (*p*-xylene), and toluene do not give any methoxylated products but afford oxidation products of the methyl groups such as aldehydes.[2a]

The above results on the HMB–O_2 CCT pairs led us to undertake further investigation on their photochemical features, particularly intervention of $C_6Me_5CH_2^+$ as well as $HMB^{+\bullet}$ as the key intermediates, in comparison with photoinduced electron transfer between DCA and HMB.

Experimental

Materials. Hexamethylbenzene (HMB, Tokyo Kasei) was crystallized twice from ethanol. In preparation of methoxymethylpentamethylbenzene ($C_6Me_5CH_2OMe$, **1a**), HMB was photochemically brominated with *N*-bromosuccinimide[5] in CCl_4 to give $C_6Me_5CH_2Br$, which was treated with NaOMe in MeOH. 9,10-Dicyanoanthracene (DCA, Tokyo Kasei) was crystallized twice from ethanol.

Absorption and Fluorescene Spectra. Absorption and fluorescence spectra were recorded with a JASCO Ubest-55 spectrophotometer and a Hitachi UV-4000 spectrofluorimeter, respectively. Fluorescence lifetimes were determined with a Horiba NAES-1100 single photon counting instrument.

Transient Absorptions. Transient absorptions were measured with 308- (Lambda Physik LPX-100 XeCl excimer laser), 355- (Spectra Physics GCR-3 Nd^{3+}–YAG laser), 360-, and 425-nm laser pulses (Lambda Physik FL-3002 dye laser pumped by the Lambda Physik LPX-100 XeCl excimer laser, DMQ and stilbene-3 dyes, respectively). The details of the apparatus for laser flash photolysis were described elsewhere.[6]

Transient Electric Conduction. Transient electric conduction was measured for a solution in a quartz rectangular cell (10 mm × 10 mm) containing two square platinum electrodes (8 mm × 8 mm) with laser beam of the appropriate wavelengths used for the measurements of transient absorptions. The measurements were carried out essentially in the same way as reported.[7]

Stationary Light Irradiation. A solution of HMB

(2.5 g, 1.5×10^{-2} mol) in a mixture (400 cm^3) of acetonitrile and methanol (1 : 1 by volume) was irradiated under oxygen atmosphere for 15 h with 313-nm light from a 400-W high-pressure mercury lamp (conversion 100%). After evaporation of the solvent, the residue was chromatographed over silica gel (CH_2Cl_2) to afford **1a** (350 mg, 12%) and 3,4,5,6-tetramethylphthalide (**2**, 400 mg, 14%).

1a: Mp 61—64 °C; ^{1}H NMR ($CDCl_3$) δ=2.20 (s, 9H), 2.30 (s, 6H), 3.40 (s, 3H), 4.48 (s, 2H); Mass *m/z* 192 (M^+), 161 (M^+-OCH_3), 160, 145.

2: IR (KBr) 1730 cm^{-1}, $\nu_{C=O}$; ^{1}H NMR ($CDCl_3$) δ=2.18 (s, 3H), 2.28 (s, 6H), 2.62 (s, 3H), 5.10 (s, 2H); Mass *m/z* 190 (M^+), 161, 133.

Similar irradiation (16 h, conversion 69%) of HMB (2.5 g) in acetonitrile–ethanol (1 : 1 by volume, 400 cm^3) gave ethoxymethylpentamethylbenzene ($C_6Me_5CH_2OEt$, **1b**, 610 mg, 28%) and **2** (70 mg, 3%).

1b: ^{1}H NMR ($CDCl_3$) δ=1.20 (t, 3H), 2.18 (s, 9H), 2.28 (s, 6H), 3.52 (q, 2H), 4.48 (s, 2H); Mass *m/z* 206 (M^+), 161 ($M^+-OCH_2CH_3$), 160, 145.

A solution of HMB (1.2 g, 7.4×10^{-3} mol) in a mixture (230 cm^3) of acetic acid and acetonitrile (1 : 6 by volume) was irradiated with 313-nm light for 8 h (conversion 98%). Silica-gel column chromatography ($CHCl_3$) of the reaction mixture after evaporation afforded pentamethylbenzyl acetate ($C_6Me_5CH_2OCOCH_3$, **1c**, 230 mg, 14%), **2** (140 mg, 10%), and pentamethylbenzyl alcohol ($C_6Me_5CH_2OH$, **3**, 230 mg, 18%).

1c: IR (KBr) 1720 cm^{-1}, $\nu_{C=O}$; ^{1}H NMR ($CDCl_3$) δ=2.02 (s, 3H), 2.12 (s, 9H), 2.18 (s, 6H), 5.20 (s, 2H); Mass *m/z* 220 (M^+), 161 ($M^+-OCOCH_3$), 160, 145.

3: ^{1}H NMR ($CDCl_3$) δ=1.20 (m, 1H), 2.24 (s, 9H), 2.36 (s, 6H), 4.78 (d, 2H); Mass *m/z* 178 (M^+), 161, 160, 145.

A solution (300 cm^3) of DCA (2×10^{-5} M, M=mol dm^{-3}) and HMB (1.5 g, 3×10^{-2} M) in CH_3CN–CH_3OH (1 : 1 by volume) was irradiated for 4 h under air with 436-nm light obtained through a bandpass filter from a 400-W high-pressure mercury lamp. The reaction mixture was treated similarly to afford **3** (5% based on HMB consumed) and pentamethylbenzaldehyde (C_6Me_5CHO, **4**, 39%). The products were identified by comparing their spectral data with those of authentic samples and quantitatively determined by GLPC (Shimadzu GC14A, GL Science TC-1 column) in comparison with an internal reference.

Results and Discussion

Absorption Spectra. A difference spectrum was obtained by subtraction of an absorption spectrum of HMB under nitrogen from that under oxygen in acetonitrile as shown in Fig. 1. The absorption observed at 300—400 nm disappeared reversibly on introduction of nitrogen to exclude oxygen. This absorption is attributable to transition of the CCT pairs of HMB–O_2.[2a)]

Reaction Products. Irradiation of the CCT pairs of HMB (ca. 0.04 M) with oxygen in acetonitrile–methanol (1 : 1 by volume) and benzene–methanol (1 : 1 by volume) with 313-nm light afforded $C_6Me_5CH_2OMe$ (**1a**, 0.12 mol based on HMB consumed) in addition to **2** (0.14 mol). Likewise, the irradiation of the CCT pairs of HMB in acetonitrile-ethanol gave $C_6Me_5CH_2OEt$ (**1b**, 0.28 mol) together with **2** (0.03 mol). The irradiation in acetonitrile–acetic acid yielded $C_6Me_5CH_2OCOCH_3$ (**1c**, 0.14 mol), **2** (0.10 mol), and $C_6Me_5CH_2OH$ (**3**, 0.18 mol) (Chart 1).

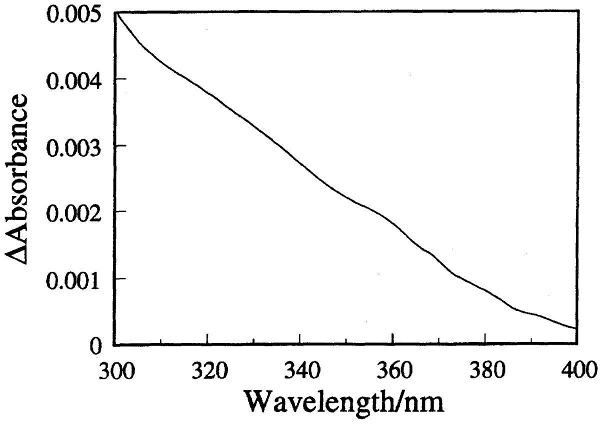

Fig. 1. A difference spectrum of HMB under oxygen (1 atm) and under nitrogen in acetonitrile.

However, irradiation of DCA in the presence of HMB (3×10^{-2} M) in aerated acetonitrile–methanol did not give **1a** at all but resulted in oxidation of the methyl group to afford **3** (0.05 mol) and C_6Me_5CHO (**4**, 0.39 mol).

Transient Absorption. DCA (7×10^{-5} M) fluorescence was effectively quenched by HMB (3×10^{-4}—1.2×10^{-3} M) with a quenching rate constant of 1.6×10^{10} M^{-1} s^{-1} (8.7×10^{9} M^{-1} s^{-1} in cyclohexane)[8)] as obtained from the observed quenching constant of 225 M^{-1} and the fluorescence lifetime of DCA, 14 ns, in acetonitrile.

Pulsed laser excitation of DCA (1×10^{-4} M) at 425 nm in the presence of HMB (0.1 M) in acetonitrile under argon or oxygen gave transient absorption spectra as depicted in Fig. 2. This figure shows absorptions around 500 and 700 nm assignable to $HMB^{+\bullet}$ (λ_{max}=498 nm)[9)]

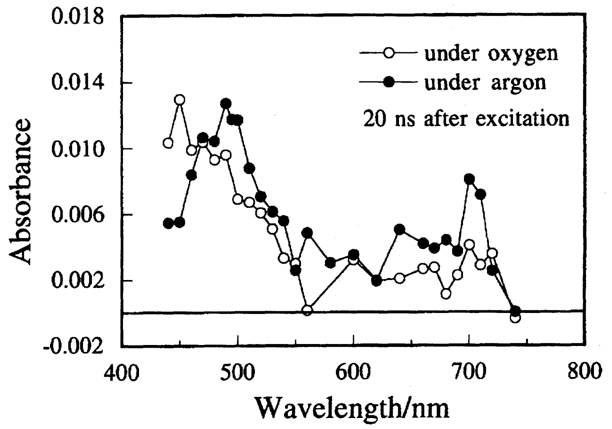

Fig. 2. Transient absorption spectra observed on excitation of DCA (1×10^{-4} M) with 425-nm laser pulses in the presence of HMB (0.1 M) in acetonitrile under argon (●) and under oxygen (○).

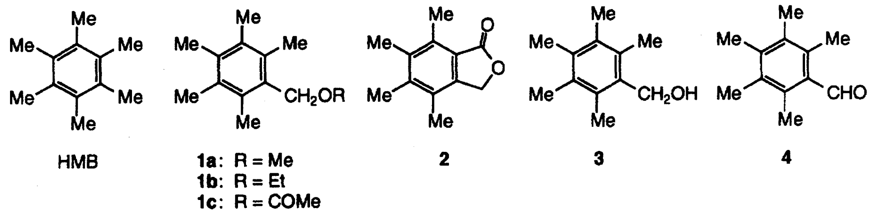

Chart 1.

and $DCA^{-\bullet}$ (λ_{max}=704 nm),[10] respectively. These absorptions decayed by second-order kinetics under argon with a half-life of 2 μs. The transient absorption simply decayed without showing any further change corresponding to subsequent deprotonation of $HMB^{+\bullet}$ into $ArCH_2^+$ ($Ar=C_6Me_5$) irrespective of its high acidity, $pK_a=-4$.[11,12] On the other hand, direct excitation of HMB (ca. 0.1 M) under oxygen in acetonitrile with 308-nm laser did not exhibit any detectable transient absorption probably due to quick deactivation of the excited species before charge separation.

Photoinduced Transient Electric Conduction. Pulsed laser excitation of DCA (1×10^{-4} M) at 425 nm in the presence of HMB (0.1 M) in acetonitrile under argon afforded a transient electric current, which decayed by second-order kinetics with a half-life of 10 μs as illustrated in Fig. 3. The observed electric conduction is attributable to the formation of $DCA^{-\bullet}$ and $HMB^{+\bullet}$.

However, an attempt to detect any observable electric conduction on excitation of the HMB–O_2 CCT pairs with 308-nm laser pulses was unsuccessful for an acetonitrile solution of HMB (2×10^{-2} M) under oxygen. Also, the pulsed laser excitation of concentrated solutions of *N*,*N*-dimethylaniline (DMA) or *N*,*N*,4-trimethylaniline (TMA) in acetonitrile (amine : solvent=1 : 9 by volume) carried out for comparison under oxygen with 360-nm laser exciting the CCT pairs failed in affording observable transient electric currents. Irradiation with 308-nm laser to excite directly the amines gave transient electric currents decaying with half-lives of 5 and 1 μs for DMA and TMA, respectively.[13] The direct excitation of the amines also afforded weak transient absorptions with poor resolution.

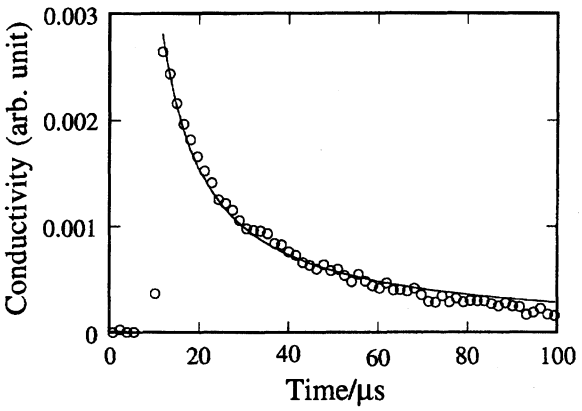

Fig. 3. A decay profile of the transient electric conduction measured on excitation of DCA (1×10^{-4} M) with 425-nm laser pulses in the presence of HMB (0.1 M) in acetonitrile. The solid line is fitted with a decay rate constant of 3.6×10^{7} M^{-1} s^{-1}.

The above failure in observing transient absorptions and transient electric conduction on excitation of the CCT pairs of oxygen with HMB as well as with *N*,*N*-dimethylanilines is probably due to very low absorbances of their CCT pairs under 1 atm (=101325 Pa) of oxygen and quick deactivation of the excited CCT pairs to the ground state in preference to charge separation.

Mechanism for Reactions of the CCT Pairs. The production of **1a**, **1b**, and **1c** on excitation of the HMB–O_2 CCT pair in a mixture of acetonitrile and the hydroxylic solvents indicates the intervention of $ArCH_2^+$ as the reactive intermediate. However, the quantum efficiencies for net chemical reactions are extremely low as reflected in the failure of direct observations of $HMB^{+\bullet}$ and $ArCH_2^+$ by transient absorption and electric conduction. The actual reactions proceed during the prolonged irradiation, and the quantum yields are too low to be exactly determined (probably lower than 10^{-4}). The results of CCT pair excitation are remarkably contrasted not only to the formation of **3** and **4** on excitation of DCA in the presence of HMB in aerated acetonitrile-methanol but also to the formation of **2** and its derivative on direct excitation of HMB under oxygen in acetonitrile–methanol.[2a)]

Figure 4 shows the energies of $(HMB\cdots O_2)^*$ and pairs of $HMB^{+\bullet}/O_2^{-\bullet}$, $ArCH_2\bullet/HO_2\bullet$, and $ArCH_2^+/HO_2^-$ with reference to the ground state of $HMB\cdots O_2$.[2b)] In the ground state of $HMB\cdots O_2$, $^3(HMB\cdots O_2)_{CT}$, the components interact very weakly with each other, i.e., to a very low extent of charge transfer. In the excited state, however, the extent of the charge transfer might increase to facilitate charge separation, particularly in polar solvents, into a radical ion pair.

The energy of $^3(HMB\cdots O_2)_{FC}{}^*$ of the Franck–Condon type is estimated to be roughly 3.2 eV based on the absorption tail around 400 nm. The relaxed excited state $^3(HMB\cdots O_2)_{CT}{}^*$ of considerable charge-transfer character is to be lower in energy than the Franck–Condon state. The radical ion pair $HMB^{+\bullet}+O_2^{-\bullet}$ is located at 2.56 eV as estimated from E_o $(HMB^{+\bullet}/HMB)=1.69$ V and E_o $(O_2/O_2^{-\bullet})=-0.87$ V vs. SCE.[14)] The contact radical ion pair $HMB^{+\bullet}\cdots O_2^{-\bullet}$ is slightly more stabilized than $HMB^{+\bullet}+O_2^{-\bullet}$ due to the Coulombic interaction. $HMB^{+\bullet}$ is highly acidic with $pK_a=-4$,[11,12)] and $O_2^{-\bullet}$

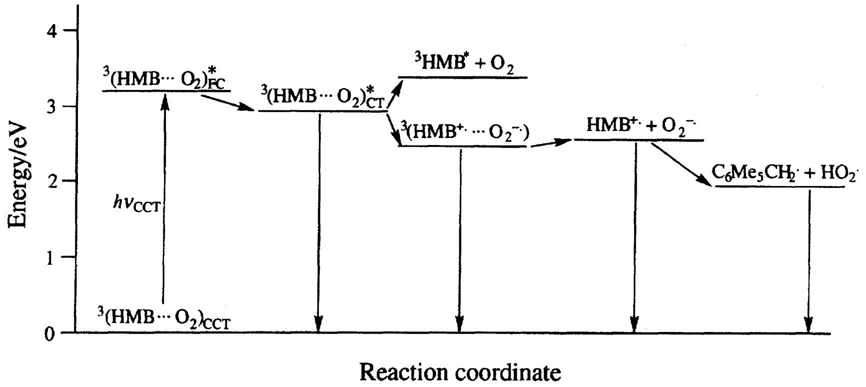

Fig. 4. Energies of reaction intermediates to be produced on excitation of CCT pairs of HMB and oxygen.

is as basic as $pK_a \cong 4$,[15,16] and therefore, the pair of $ArCH_2\cdot + HO_2\cdot$ is estimated to be 0.48—0.72 eV more stable than $HMB^{+\cdot} + O_2^{-\cdot}$ as previously argued.[17] Thus, the conversion of $^3(HMB\cdots O_2)^*$ to $HMB^{+\cdot} + O_2^{-\cdot}$ and $ArCH_2\cdot + HO_2\cdot$ is energetically favorable but proceeds with a very low efficiency, since $^3(HMB\cdots O_2)^*$ mostly deactivates to the ground state.

The deactivation of $^3(HMB\cdots O_2)^*$ seems not to give efficiently the HMB triplet ($^3HMB^*$, $E_T = 78.1$ $kcal\,mol^{-1} = 3.40$ eV)[18] because of endothermicity of this process in contrast to the cases of the excited 1-methylnaphthalene–O_2[19] and 1,2,3,4-tetramethylnaphthalene–O_2 CCT pairs.[2c] If $^3HMB^*$ were produced, it would undergo energy transfer to oxygen to give singlet oxygen which would act on HMB to give the hydroperoxy-endoperoxide as observed on dye-sensitization of HMB in the presence of oxygen.[3] However, the peroxide was not produced from the excitation of the HMB–O_2 CCT pairs.

Since the oxidation potential of $ArCH_2\cdot$ could be around 0.5 V vs. SCE[2b] and $HO_2\cdot$ is reported to have a considerably large electron affinity of 1.16[17] or 1.85 eV,[20] the electron transfer from $ArCH_2\cdot$ to $HO_2\cdot$ can feasibly take place in competition with their recombination. The failure in direct observation of $HMB^{+\cdot}$ or $ArCH_2^+$ on pulsed laser excitation of the HMB–O_2 CCT pairs in spite of the formation of products arising from $ArCH_2^+$ is reasonably attributed to a very low absorbance of the HMB–O_2 CCT pairs and very facile deactivation of their excited state.

The excitation of DCA in the presence of HMB gave $HMB^{+\cdot}$ and $DCA^{-\cdot}$, as observed by their transient absorption, but did not produce the products due to $ArCH_2^+$. It is only the oxidation of the methyl group that was observed. Radical anion $DCA^{-\cdot}$ undergoes electron transfer to oxygen to yield $O_2^{-\cdot}$.[21] Therefore, in the DCA–HMB–O_2 system, the formed $HMB^{+\cdot}$ may react with $O_2^{-\cdot}$ or molecular oxygen through diffusional encounter. On the contrary, on excitation of the HMB–O_2 CCT pair, $HMB^{+\cdot}$ and $O_2^{-\cdot}$ may interact in a very close proximity to afford $ArCH_2^+$. The results of the DCA–HMB system suggest that the resulting $HMB^{+\cdot}$ reacts more efficiently with oxygen than with $O_2^{-\cdot}$ or the diffusional encounter between $HMB^{+\cdot}$ and $O_2^{-\cdot}$ leads to reverse electron transfer from $O_2^{-\cdot}$ to $HMB^{+\cdot}$ in a different way from their geminate pairs.

References

1) M. Tamres and R. L. Strong, "Molecular Association," ed by R. Foster, Academic Press, London (1979), Vol, 2, pp. 397—416, and references cited therein.

2) a) K. Onodera, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **21**, 2831 (1980); b) K. Onodera, G. Furusawa, M. Kojima, M. Tsuchiya, S. Aihara, R. Akaba, H. Sakuragi, and K. Tokumaru, *Tetrahedron*, **41**, 2215 (1985); c) H. Sakuragi, G. Furusawa, K. Ueno, and K. Tokumaru, *Chem. Lett.*, **1982**, 1213; d) M. Kojima, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **22**, 2889 (1981); e) R. Akaba, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **25**, 665 (1984).

3) C. J. M. van den Heuvel, H. Steinberg, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **96**, 157 (1977); C. J. M. van den Heuvel, A. Hofland, H. Steinberg, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **99**, 275 (1980).

4) H. H. Wasserman, P. S. Mariano, and P. M. Keehn, *J. Org. Chem.*, **36**, 1765 (1971).

5) F. Vogtle, M. Zuber, and R. G. Lichtenthaler, *Chem. Ber.*, **106**, 717 (1973).

6) H. Okamoto, T. Arai, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **63**, 2881 (1990).

7) T. Hino, H. Akazawa, H. Masuhara, and N. Mataga, *J. Phys. Chem.*, **80**, 33 (1976); Y. Hirata, Y. Kanda, and N. Mataga, *J. Phys. Chem.*, **87**, 1659 (1983).

8) G. Jones, II, and S.-H. Chiang, *Tetrahedron*, **37**, 3397 (1981).

9) T. Shida, "Electronic Absorption Spectra of Radical Ions," (Physical Science Data 34)," Elsevier, Amsterdam (1988).

10) I. R. Gould, D. Ege, J. E. Moser, and S. Farid, *J. Am. Chem. Soc.*, **112**, 4290 (1990).

11) J. Barek, E. Ahlberg, and V. D. Parker, *Acta Chem. Scand., Ser. B.*, **B34**, 85 (1980).

12) E. Baciocchi, M. Mattioli, R. Romano, and R. Ruzziconi, *J. Org. Chem.*, **56**, 7154 (1991).

13) The formation of short-lived radical cations of DMA was observed by the conventional flash photolysis using a wide range of wavelength of light to excite DMA in polar solvents: M. Hori, H. Itoi, and H. Tsubomura, *Bull. Chem.*

Soc. Jpn., **43**, 3765 (1970).

14) D. T. Sawyer, G. Chiericato, Jr., C. T. Angelis, E. J. Nanni, Jr., and T. Tsuchiya, *Anal. Chem.*, **54**, 1720 (1982).

15) G. Czapsi and B. H. J. Bielski, *J. Phys. Chem*, **67**, 2180 (1963).

16) J. Rabani and S. O. Nielsen, *J. Phys. Chem.*, **73**, 3736 (1969).

17) V. M. Bierbaum, R. J. Schmitt, C. H. DePuy, R. D. Mead, P. A. Schulz, and W. C. Lineberger, *J. Am. Chem. Soc.*, **103**, 6262 (1981).

18) S. L. Murov, I. Carmichael, and G. L. Hug, "Handbook of Photochemistry," 2nd ed, Marcel Dekker, New York (1993), p. 95.

19) S. L. Logunov and M. A. J. Rodgers, *J. Phys. Chem.*, **96**, 2915 (1992); **97**, 5643 (1993).

20) S. W. Benson and P. S. Nangia, *J. Am. Chem. Soc.*, **102**, 2843 (1980).

21) L. T. Spada and C. S. Foote, *J. Am. Chem. Soc.*, **102**, 391 (1980).