

Fluorescence Measurement of 3,5-Dimethoxyphenol Radical Cation Generated by Pulse Radiolysis in 1,2-Dichloroethane

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Radical cation of 3,5-dimethoxyphenol in the excited state generated in 1,2-dichloroethane solution by the tandem irradiation of 28-MeV electron and 532-nm laser pulses emitted fluorescence around 600–750 nm with a quantum yield of 2.0×10^{-3} .

Radical ions are an important intermediate in various electron transfer reactions in solution or heterogeneous systems such as photoinduced electron transfer or radiation chemical reactions. Their chemical and physical properties have been intensively studied for these three decades. On the other hands, fewer physical and chemical properties of excited radical ions have been revealed as compared to excited radicals.^{1–7} This could be attributed to the weakly or non-fluorescent nature and extremely short lifetime of excited radical ions. Whereas lifetime of excited radicals lies in the range of a few tens to hundreds nanoseconds and many of excited radicals fluoresce, that of excited radical ions is typically much shorter than 1 ns and fluorescence in solution has been reported for only a few excited radical ions.^{2,5–7} Such behavior has been explained by their low excitation energy which allows fast nonradiative internal conversion for the sake of the energy gap law.² We have recently reported laser-induced transient fluorescence of 1,3,5-trimethoxybenzene (TMB) radical cation ($\text{TMB}^{+\bullet}$) which is generated in acetonitrile at room temperature by laser flash photolysis.^{7a} If strong fluorescence of a radical ion is observed, it will be a help for the monitor of electron transfer phenomena in homogeneous and heterogeneous environment with a high sensitivity. We have studied laser-induced fluorescence of radical cations generated by pulse radiolysis in order to find “fluorescent radical ion probe” and have found that 3,5-dimethoxyphenol (DMP) radical cation ($\text{DMP}^{+\bullet}$) showed a fluorescence stronger than $\text{TMB}^{+\bullet}$ in 1,2-dichloroethane (DCE) solution.

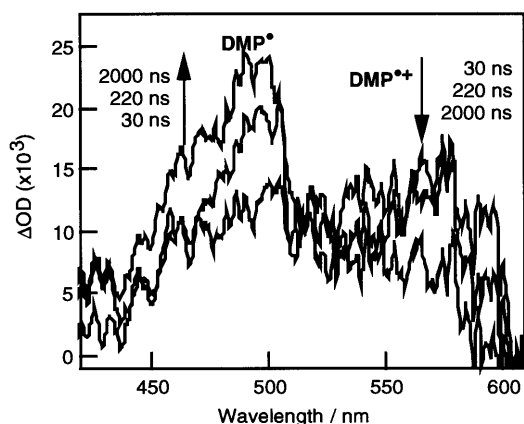
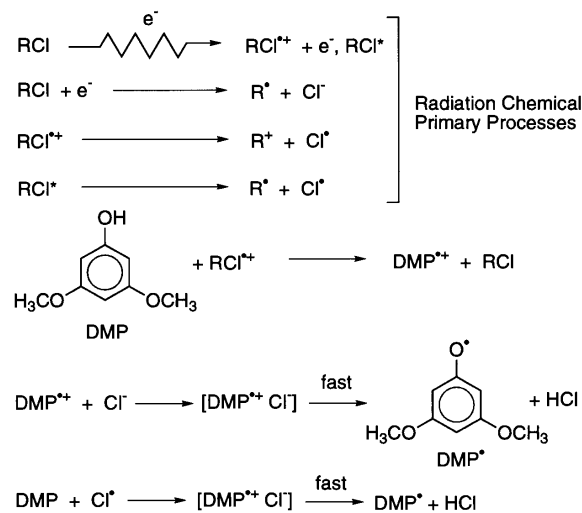


Figure 1. Time-resolved absorption spectra of an Ar-saturated 1,2-dichloroethane (DCE) solution containing DMP (5.0×10^{-3} M) measured at 30, 220, and 2000 ns (gate time: 30 ns) after the electron pulse.

A transient absorption spectrum around 575 nm was observed immediately after the 8-ns electron pulse irradiation of DMP (5.0×10^{-3} M) in argon-purged DCE.⁸ The spectrum in DCE is similar to that observed by laser flash photolysis of DMP in acetonitrile and is assigned to $\text{DMP}^{+\bullet}$.⁹ The time-resolved transient absorption spectra showed a slow growth of a new peak at 500 nm (Figure 1). This peak was assigned to 3,5-dimethoxyphenoxy radical (DMP^{\bullet}) according to Johnston et al.⁹ The absorption around 575 nm due to $\text{DMP}^{+\bullet}$ decreased with time and most of $\text{DMP}^{+\bullet}$ disappeared at 2 μs after the electron pulse to give DMP^{\bullet} through deprotonation of $\text{DMP}^{+\bullet}$. It has been shown that bimolecular deprotonation of $\text{DMP}^{+\bullet}$ occurs to give DMP^{\bullet} in the presence of basic reagents.⁹ The growth of DMP^{\bullet} monitored at 472 nm corresponded to the decay of the transient absorption at 575 nm. A rapid decay of $\text{DMP}^{+\bullet}$ and growth of DMP^{\bullet} were observed in their time profiles within 20 ns. These would be due to the electron transfer reaction of DMP with chlorine atom (Cl^{\bullet}) as a byproduct of pulse radiolysis of DCE.^{7b} We attribute the basic species for the deprotonation to Cl^- which is generated by the radiation chemical primary processes of DCE. The plausible mechanism involved therein is summarized in Scheme 1.



Scheme 1.

We have tried to measure the fluorescence from excited $\text{DMP}^{+\bullet}$ ($\text{DMP}^{+\bullet*}$) to examine whether the symmetrical substitution as in TMB is required for fluorescence emission and unimolecular deprotonation from $\text{DMP}^{+\bullet*}$ competes with radiative transition or not. Excitation of $\text{DMP}^{+\bullet}$ at 532 nm with the 2nd harmonic pulse of Nd:YAG laser gave broad fluorescence around 600–750 nm (Figure 2). The fluorescence spectrum showed a mirror image symmetry to the absorption spectrum of $\text{DMP}^{+\bullet}$. The integrated fluorescence intensity decreased with the

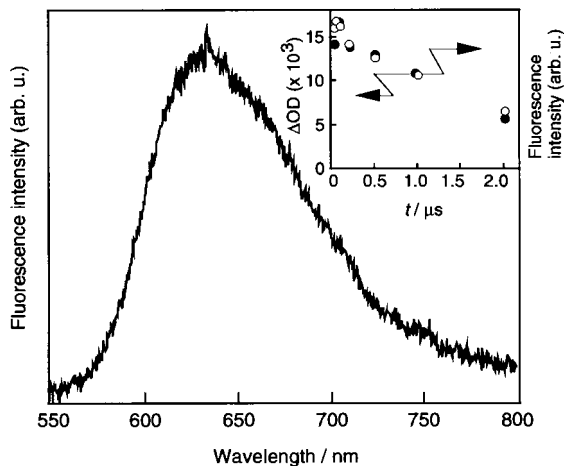
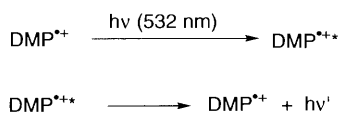


Figure 2. Fluorescence spectrum of DMP** measured at 100 ns after the electron pulse. Excitation wavelength: 532 nm and energy: 130 mJ pulse⁻¹. Insert: plot of the integrated fluorescence intensity of DMP** as a function of the delay time of the 532-nm laser pulse relative to the electron pulse is superimposed with plot of the transient absorption at 575 nm.

increase of the delay time of the laser pulse relative to the electron pulse in a similar manner to the temporal profile of the transient absorption monitored at 575 nm (Figure 2). This also supports the assignment of the fluorescence to that of DMP**. When DMP⁺ was excited with the 532-nm laser pulse, the absorption of DMP⁺ was unchanged and no increase of that of DMP^{*} was observed.



The fluorescence quantum yield (Φ_f) of DMP** in DCE was independent of the delay time being $(2 \pm 0.3) \times 10^{-3}$ except for that at 30 ns (1.3×10^{-3}). The low fluorescence quantum yield at 30 ns may be resulted from intra-cage quenching of [DMP** Cl⁻]. The $\Phi_f = (2 \pm 0.3) \times 10^{-3}$ for DMP** was higher than that for free TMB** (1.1×10^{-3}) in DCE.¹⁰ We also estimated the radiative rate constant (k_f) for DMP** to be $k_f = 5.8 \times 10^6 \text{ s}^{-1}$ as did in the previous report using the Strickler–Berg relationship.^{7a} Although the value of k_f is smaller than that for TMB** ($9.5 \times 10^6 \text{ s}^{-1}$), Φ_f was larger by a factor of 1.8. It is suggested that nonradiative process in DMP** is slower by a factor of 3.0 as compared to TMB**. Since deprotonation from DMP** is not an important process for the nonradiative process, methyl group would play an important role in the non-radiative decay of DMP** and TMB** as reported for alkyl-benzenes in the singlet excited states.¹¹ Lifetime of DMP** can be estimated from Φ_f to be $\approx 350 \text{ ps}$ from eq 1,

$$\Phi_f = k_f / (k_f + k_{nr}) = k_f \tau \approx k_f / k_{nr} \quad (1)$$

where k_{nr} is the rate constant for the nonradiative decay.

The fluorescent nature of TMB** was previously attributed partially to its pseudo-D_{3h} structure which makes the D₀ and D₁ states degenerate to allow the D₂–D₀ fluoresce as has been discussed for 1,3,5-trifluorobenzene radical cation in the gas phase.¹² The fluorescent nature of DMP** ruled out the necessity of complete C₃-symmetric substitution of the benzene-ring and suggested a possibility in expansion of the 1,3,5-trioxybenzene family as fluorescent radical cation probes for the detection of hole or electron transfer phenomena.

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References and Notes

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- An argon-purged 4-mL portions of DCE solution of DMP was placed in a quartz cuvette ($1 \times 1 \times 4 \text{ cm}^3$) and was irradiated with an electron pulse (28 MeV, 8 ns). The radiolytically generated radical cations were excited with a second harmonic pulse (532 nm, 130 mJ pulse⁻¹) of an Nd:YAG laser (Quantel Brilliant) with a delay time of -100 – 2000 ns relative to the electron pulse. The obtained fluorescence spectra are not corrected for the wavelength dependence of the system. The details are described in the previous paper.^{7b}
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- Since TMB⁺ tends to form an ion pair with Cl⁻, free TMB⁺ was generated by secondary electron transfer to biphenyl radical cation (BP⁺) by the addition of BP 10 times as much as TMB.^{7b} The excitation was performed within 100 ns after the electron pulse.
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