JOC Article

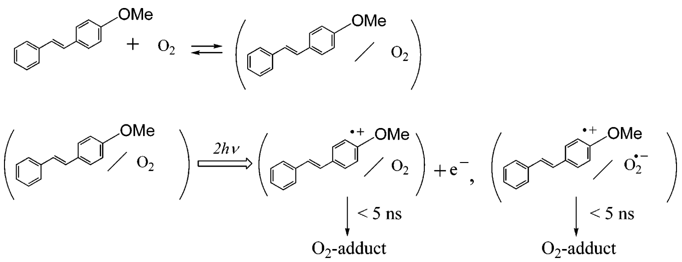
Effect of Oxygen on the Formation and Decay of Stilbene Radical Cation during the Resonant Two-Photon Ionization

Michihiro Hara, Shingo Samori, Cai Xichen, Mamoru Fujitsuka, and Tetsuro Majima*

The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

majima@sanken.osaka-u.ac.jp

Received February 19, 2005



Formation and decay of radical cations of *trans*-stilbene and *p*-substituted *trans*-stilbenes ($\mathbf{S}^{\bullet+}$) during the resonant two-photon ionization (TPI) of **S** in acetonitrile in the presence and absence of O_2 have been studied with laser flash photolysis using a XeCl excimer laser (308 nm, fwhm 25 ns). The transient absorption spectra of $\mathbf{S}^{\bullet+}$ were observed with a peak around 470−490 nm. The formation quantum yield of $\mathbf{S}^{\bullet+}$ (0.06−0.29) increased with decreasing oxidation potential (E^{ox}) and increasing fluorescence lifetime (τ_f) of **S**, except for *trans*-4-methoxystilbene which has the lowest E^{ox} and longer τ_f among **S**. The considerable low yield and fast decay in a few tens of nanoseconds time scale were observed for *trans*-4-methoxystilbene$^{\bullet+}$ in the presence of O_2, but not for other $\mathbf{S}^{\bullet+}$. It is suggested that formation of the ground-state complex between *trans*-4-methoxystilbene and O_2 and the distonic character of *trans*-4-methoxystilbene$^{\bullet+}$ with separation and localization of the positive charge on the oxygen of the *p*-methoxyl group and an unpaired electron on the *β*-olefinic carbon are responsible for the fast reaction of *trans*-4-methoxystilbene$^{\bullet+}$ with O_2 or superoxide anion, leading to the considerable low yield and fast decay of *trans*-4-methoxystilbene$^{\bullet+}$. The mechanism based on the transient absorption measurement of $\mathbf{S}^{\bullet+}$ during the TPI is consistent with the relatively high oxidation efficiency of *trans*-4-methoxystilbene among **S** based on the product analysis during the photoinduced electron transfer in the presence of a photosensitizer such as 9,10-dicyanoanthracene and O_2 in acetonitrile.

Introduction

Radical cations can be generated from one-electron oxidation such as electrochemical reaction, chemical oxidation using one-electron oxidants, photoinduced electron transfer, resonant two-photon ionization (TPI), and radiation chemical reaction. The properties and reactions of radical cations have been extensively investigated.[1−5] Since most of radical cations are highly reactive intermediates, they decompose unimolecularly or react bimolecularly with other molecules such as hole transfer, addition, and neutralization. For example, the nucleophilic addition to radical cations is well-known to occur to give the corresponding adducts because of the cationic character. On the other hand, the bimolecular reactivity of radical cations as radicals is rather rare.

Radical cations of stilbene (**St**) and stilbene derivatives (**S**)[1,4−7] react with various necleophiles. On the other hand, most $\mathbf{S}^{\bullet+}$ react slowly with O_2 at the bimolecular

---

* Corresponding author. Tel: +81-6-6879-8495. Fax: +81-6-6879-8499.

[1] Fox, M. A. *Chem. Rev.* **1979**, *79*, 253.

[2] Fox, M. A. In *Photoinduced Electron Transfer*; Chanon, M., Ed.; Elsevier: Amsterdam, 1988.

[3] Eberson, L. *Electron-Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987.

[4] Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425.

[5] Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

[6] Lewis, F. D.; Letsinger, R. L.; Wasielewski, M. R. *Acc. Chem. Res.* **2001**, *34*, 159.

[7] Baciocchi, E.; Bietti, M.; Salamone, M.; Steenken, S. *J. Org. Chem.* **2002**, *67*, 2266.

10.1021/jo050317n CCC: $30.25 © 2005 American Chemical Society

Published on Web 04/20/2005

TABLE 1. Properties of S and S$^{\bullet+}$ and Formation of S$^{\bullet+}$ during the TPI Using the 308-nm XeCl Excimer Laser[a]

		absorption		fluorescence		formation of **S**$^{\bullet+}$			
S	E^{ox}/V	λ_{max}/nm	ϵ_{max}/M^{-1} cm^{-1}	λ_{max}/nm	τ_f/ps	λ_{max}/nm	ϵ_{max}/M^{-1} cm^{-1}	Φ_{ion}	slope
St	1.27	307	3.3×10^4	349	44	472	6.0×10^4	2.0×10^{-3}	1.9
MeSt	1.11	299	2.2×10^4	352	45	485	6.7×10^4	1.9×10^{-3}	2.0
MeOSt	0.90	317	2.5×10^4	373	64	480	6.1×10^4	0.6×10^{-3} 2.4×10^{-3b}	2.0
ClSt	1.23	296	3.7×10^4	374	66	490	6.9×10^4	2.9×10^{-3}	1.7
CNSt	1.39	323	3.7×10^4	378	32	485	5.1×10^4	1.1×10^{-3}	1.9

[a] Peak voltage for the irreversible oxidation wave vs Ag/Ag$^+$ was taken as oxidation potentials (E^{ox}), absorption peak wavelength (λ_{max}), molar absorption coefficient of the peak (ϵ_{max}), fluorescence peak (λ_{max}), and lifetime (τ_f) of **S**, λ_{max} and ϵ_{max} of the transient absorption of **S**$^{\bullet+}$, formation quantum yields of **S**$^{\bullet+}$ (Φ_{ion}), and slope of log−log plots of concentration of **S**$^{\bullet+}$ against F in J cm^{-2}. [b] In Ar-saturated AN solution.

rate constant of $<10^6$ M^{-1} s^{-1}.[8,9] However, *trans*-4-methoxystilbene$^{\bullet+}$ reacts much faster with O$_2$ at the bimolecular rate constant of (0.9−4.5) × 10^7 M^{-1} s^{-1} because of its distonic character.[9] Several **S**$^{\bullet+}$ react with superoxide anion ($O_2^{\bullet-}$), generated from photoinduced electron-transfer reaction of an acetonitrile (AN) solution of **S** and a photosensitizer such as 9-cyanoanthracene, 9,10-dicyanoanthracene, and chloranil in the presence of O$_2$, at almost diffusion-controlled rate, to yield two aromatic aldehydes as the stable products via cycloreversion of the dioxetane intermediates.[8−12]

The TPI of organic molecules (M) occurs to give M$^{\bullet+}$ and an electron with irradiation at a high laser fluence (F in J cm^{-2}) using an intense short-pulsed laser with a wavelength tuned to the M absorption,[13−25] when M has relatively low oxidation potentials (E^{ox}) or ionization potential (IP) and strong absorption at the laser wavelength. We have studied the TPI of various M[26,27] and elucidated the dependence of the formation efficiency of M$^{\bullet+}$ on solvents, fluorescence lifetime (τ_f), and E^{ox} of M and effect of cyclodextrines including M.[26]

In the present paper, we have studied the formation and decay of **S**$^{\bullet+}$ during the TPI of **S** in AN in the presence and absence of O$_2$ using a XeCl laser flash (308 nm, 50−200 mJ pulse^{-1}, F= 128−512 J cm^{-2}, 25-ns fwhm), and found that the *trans*-4-methoxystilbene radical cation is considerably quenched by O$_2$ or $O_2^{\bullet-}$ in a few tens ns time scale, but not for other **S**.

Experimental Section

St, *trans*-4-methylstilbene (**MeSt**), *trans*-4-methoxystilbene (**MeOSt**), *trans*-4-chlorostilbene (**ClSt**), and *trans*-4-cyanostilbene (**CNSt**) were prepared according to the procedures previously reported.[26] AN (spectroscopic grade) was used without further purification. Measurements of UV/vis spectra, fluorescence spectra, and oxidation potentials (E^{ox}) of **S** were carried out as described in our previous report.[26] Such spectral data and E^{ox} are summarized in Table 1.

The τ_f values of **S** were measured by a single photon counting method using a streak scope. The samples were excited with third harmonic generation (287 nm) of a Ti: sapphire laser (fwhm 100 fs) equipped with a pulse selector and harmonic generator.

Laser flash photolysis was carried out using a XeCl excimer laser (308 nm, 25 ns, 200 mJ pulse^{-1}) or Nd:YAG laser (355 nm, 5 ns, 60 mJ pulse^{-1}) as an excitation source. The monitor light was obtained from a 450-W Xe lamp synchronized with the laser flash. The irradiation volume of the laser beam was identical with that of the monitor light source. The intensity of the monitor light source was detected using a photomultiplier. The signal from the photomultiplier was digitized by an oscilloscope and transmitted to a personal computer via the RS 232C interface. Transient absorption spectra were measured by a multichannel analyzer with an image intensifier having a 30-ns gate width and transmitted to a personal computer via the RS 232C interface. Air-saturated AN solutions containing **S** were prepared in a transparent rectangular cell made of quartz (1.0 × 1.0 × 4.0 cm, optical path length of 1.0 cm). The concentration of **S** was adjusted to have an absorbance of 1.0 at 308 nm of the excitation laser wavelength. All data during the laser flash photolysis were measured with a single laser shot on a fresh sample in order to avoid sample degradation. All spectral measurements, transient absorption measurements, and oxidation potential measurements were carried out at room temperature.

Results

Formation of S$^{\bullet+}$ during the TPI with a 308-nm 25-ns Laser Flash. A transient absorption spectrum with a peak at 472 nm was observed during the 308-nm XeCl laser flash photolysis of **St** in air-saturated AN (3.8 × 10^{-5} M) at F = 512 mJ cm^{-2} (Figure 1). The optical density (ΔOD) of the transient absorption increased with increasing F. The transient absorption spectrum was reasonably assigned to **St**$^{\bullet+}$ according to our previous

---

(8) Tsuchiya, M.; Ebbesen, T. W.; Nishimura, Y.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1987**, 2121.

(9) Majima, T.; Tojo, S.; Ishida, A.; Takamuku, S. *J. Org. Chem.* **1996**, *61*, 1, 7793.

(10) Eriksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455.

(11) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083.

(12) Lewis, F. D.; Bedell, A. M.; Dykstra, R. E.; Elbert, J. E.; Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 8055.

(13) Saito, F.; Tobita, S.; Shizuka, H. *J. Photochem. Photobiol. A* **1997**, *106*, 119.

(14) Schmidt, K. H.; Sauer, M. C., Jr.; Lu, Y.; Liu, A. *J. Phys. Chem.* **1990**, *94*, 244.

(15) Shafirovich, V.; Dourandin, A.; Huang, W.; Luneva, N. P.; Geacintov, N. E. *J. Phys. Chem. B* **1999**, *103*, 10924.

(16) Hirata, Y.; Mataga, N.; Sakata, Y.; Misumi, S. *J. Phys. Chem.* **1986**, *90*, 6065.

(17) Thomas, J. K.; Richards, J. T.; West, G. *J. Phys. Chem.* **1970**, *74*, 4137.

(18) Piciulo, P. L.; Thomas, J. K. *J. Chem. Phys.* **1978**, *68*, 3260.

(19) Nakabayashi, T.; Kamo, S.; Sakuragi, H.; Nishi, N. *J. Phys. Chem. A* **2001**, *105*, 8605.

(20) Braun, C. L.; Scott, T. W. *J. Phys. Chem.* **1983**, *87*, 4776.

(21) Faria, J. L.; Steenken, S. *J. Phys. Chem.* **1993**, *97*, 1924.

(22) Braun, C. L.; Scott, T. W. *J. Phys. Chem.* **1987**, *91*, 4436.

(23) Mori, Y.; Yoneda, A.; Shinoda, H.; Kitagawa, T. *Chem. Phys. Lett.* **1991**, *183*, 584.

(24) Kellmann, A.; Tfibel, F. *Chem. Phys. Lett.* **1980**, *69*, 61.

(25) Johnston, L. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1993**, *115*, 6564.

(26) Hara, M.; Tojo, S.; Majima, T. *J. Photochem. Photobiol. A* **2004**, *162*, 121.

(27) Hara, M.; Tojo, S.; Kawai, K.; Majima, T. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3215.

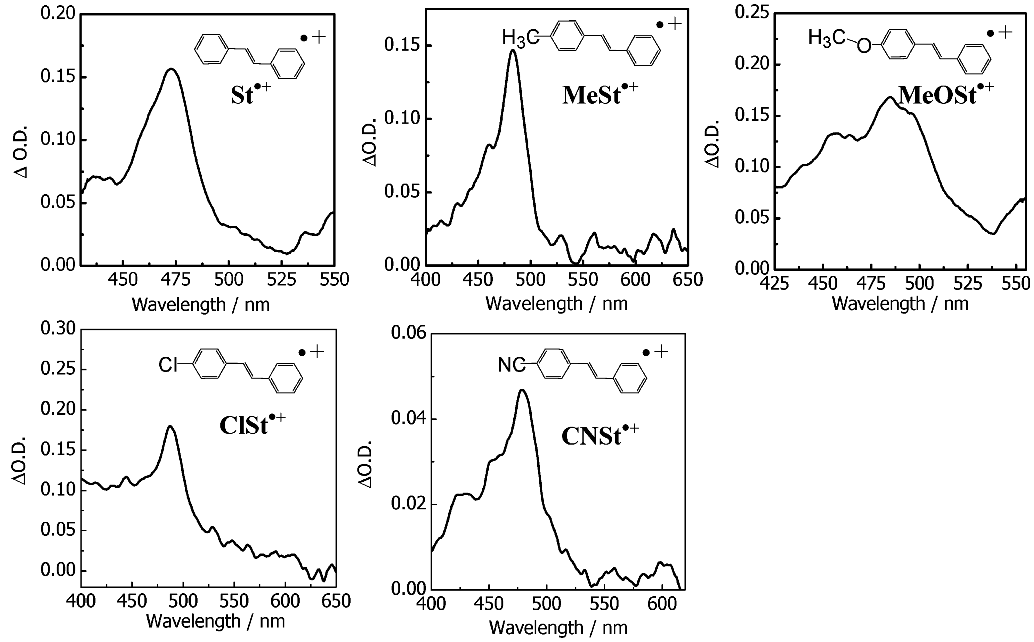


FIGURE 1. Transient absorption spectra of $S^{\bullet+}$ observed at 500 ns after a laser flash with $F = 512$ mJ cm^{-2} $pulse^{-1}$ during the TPI of **S** using a 308-nm XeCl excimer laser in air-saturated AN. Concentrations of **St**, **MeSt**, **MeOSt**, **ClSt**, and **CNSt** were 3.8×10^{-5}, 5.0×10^{-5}, 4.0×10^{-5}, 3.1×10^{-5}, and 3.3×10^{-5} M, respectively.

report.[12,26] From the relationship between the ionization potential (IP) of **St** (7.8 eV)[28] and the photon energy of XeCl laser (4.0 eV), **St** is ionized by two-photon excitation during the 308-nm laser flash photolysis. Similar transient absorption spectra of $\mathbf{S}^{\bullet+}$ with a peak around 470–490 nm were observed during the TPI of **S** with a 308-nm laser flash in air-saturated AN (eq 1)

$$\mathbf{S} + 2h\nu\ (308\ \text{nm}) \rightarrow \mathbf{S}^{\bullet+} + e^- \qquad (1)$$

An electron generated together with $\mathbf{S}^{\bullet+}$ reacts with AN to give an AN radical anion ($AN^{\bullet-}$) and the dimer radical anion ($(AN)_2^{\bullet-}$), which have a weak absorption in the range of 400–600 nm.[29] Even when the solvated electron reacts partly with **S** (10^{-5} M) at the diffusion-controlled rate constant of (2–5) $\times$ 10^{10} M^{-1} s^{-1},[30] **S** radical anion can be negligible in the time scale of 100 ns. In fact, no transient absorption of **St** radical anion with a peak at 530 nm was observed at 100 ns after the laser flash during the TPI of **St** (3.8×10^{-5} M) in air-saturated AN as shown in Figure 1.

All $\mathbf{S}^{\bullet+}$ have a relatively sharp absorption peak around 470–490 nm except for $\mathbf{MeOSt}^{\bullet+}$. The broad absorption of $\mathbf{MeOSt}^{\bullet+}$ may correspond to the distonic character with separation and localization of the positive charge on the oxygen of the *p*-methoxyl group and an unpaired electron on the β-olefinic carbon.[9]

From $\Delta OD_{480} = 0.15$ at 500 ns after the laser shot and the molar absorption coefficient of $\mathbf{St}^{\bullet+}$ at 480 nm ($\epsilon_{480} = 4.7 \times 10^4$ M^{-1} cm^{-1}), which was estimated from the hole transfer from biphenyl radical cation to **St** during the laser flash photolysis of a mixture of **St** (3.8×10^{-5} M), 9,10-dicyanoanthracene (1 mM), and biphenyl (0.1 M) in air-saturated AN, the concentration of $\mathbf{St}^{\bullet+}$ ($[\mathbf{St}^{\bullet+}]$) was calculated to be 2.0×10^{-6} M. The number of laser photons absorbed by **St** (N_p) was measured to be 2.8×10^{-4} einstein L^{-1} from the laser intensity.[31] The formation quantum yield of $\mathbf{St}^{\bullet+}$ ($\Phi_{ion} = [\mathbf{St}^{\bullet+}]/N_p$) under the conditions of Figure 1 was calculated to be 2.0×10^{-3}. Similarly, Φ_{ion} values for other **S** were obtained as shown in Table 1.

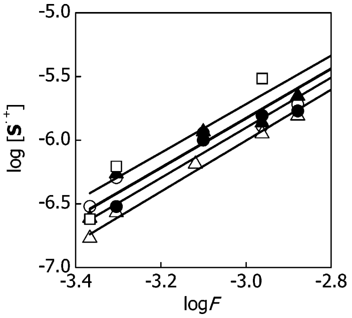


FIGURE 2. Log–log plots of $[\mathbf{S}^{\bullet+}]$ (in M) vs laser fluence (F in J cm^{-2} $pulse^{-1}$) during the TPI using the 308-nm XeCl excimer laser. $[\mathbf{S}^{\bullet+}]$ values were calculated from ΔOD at the absorption peak observed immediately after the laser flash: $\mathbf{St}^{\bullet+}$(○), $\mathbf{MeSt}^{\bullet+}$(●), $\mathbf{MeOSt}^{\bullet+}$(□), $\mathbf{ClSt}^{\bullet+}$(▲), and $\mathbf{CNSt}^{\bullet+}$(□).

The log–log plots of $[\mathbf{St}^{\bullet+}]$ vs F showed linear relationships with the slope of approximately 2 (Table 1), indicating that the yield of $\mathbf{St}^{\bullet+}$ is proportional to F^2 (Figure 2). The slope of approximately 2 was also obtained for other **S**, indicating two-photon excitation during the TPI of **S**.

Relationship between Φ_{ion} and Properties of S such as E^{ox} and τ_f. Effects of properties of **S** such as E^{ox}

---

(28) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(29) Bell, I. P.; Rodgers, M. A. J.; Burrows, H. D. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 315.

(30) Majima, T.; Fukui, M.; Ishida, A.; Takamuku, S. *J. Phys. Chem.* **1996**, *100*, 8913.

(31) Hara, M.; Sunagawa, T.; Oseki, Y.; Majima, T. *J. Photochem. Photobiol. A* **2004**, *163*, 153.

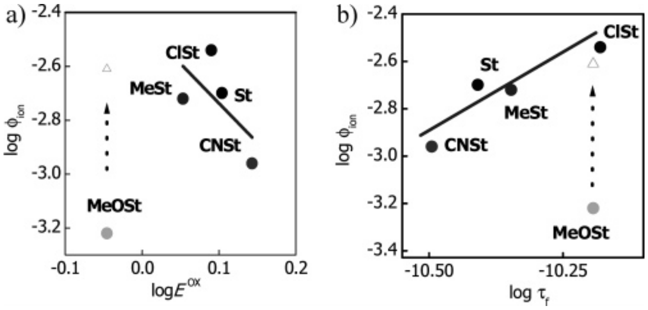


FIGURE 3. Plots of log Φ_{ion} vs log E^{ox} (a) and vs log τ_f (b) during the TPI of **S** in air- (○) and Ar-saturated (△) AN solutions using a 25-ns 308-nm XeCl excimer laser.

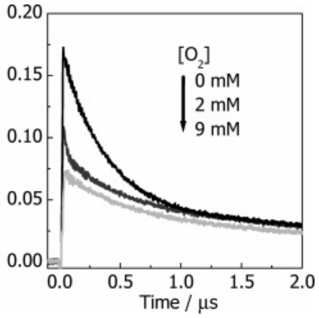


FIGURE 4. Time profiles of the transient absorption of **MEOST**$^{\bullet+}$ at 480 nm during the 355-nm TPI of **MeOST** in Ar-, air-, and O$_2$-saturated AN (O$_2$ concentration of 0, 2, and 9 mM, respectively) using a 355-nm Nd^{3+}:YAG laser (5-ns, 60 mJ pulse^{-1}, 212 mJ cm^{-2}).

and τ_f of **S** in the lowest singlet excited state (**S**(S$_1$)) on Φ_{ion} were examined. Linear relations between the logΦ_{ion} (Φ_{ion} = 0.06−0.29) and logE^{ox} of **S** or logτ_f of **S**(S$_1$) were observed (Figure 3), except for **MeOSt** in air-saturated AN solution. In other words, Φ_{ion} increased with decreasing E^{ox} and increasing τ_f, except for **MeOSt** in air-saturated AN solution.

Decay of S$^{\bullet+}$ during the TPI with a 355-nm 5-ns Laser Flash. The decay profiles of the transient absorption of **MeOSt**$^{\bullet+}$ at 480 nm were measured in Ar-, air-, and O$_2$-saturated AN (5.6×10^{-3} M) during the 355-nm TPI of **MeOSt** using a Nd^{3+}:YAG laser (Figure 4). The ΔOD$_{480}$ values observed immediately after the 5-ns laser flash depended on the concentration of O$_2$. The decay of ΔOD$_{480}$ in the time scale of 1 μs in the absence of O$_2$ was analyzed by the second-order kinetics for the reaction of **MeOSt**$^{\bullet+}$ with AN$^{\bullet-}$ and (AN)$_2^{\bullet-}$ at the rate constant of approximately 10^{13} M^{-1} s^{-1}. The decay of ΔOD$_{480}$ in the time scale of a few microseconds in the absence and presence of O$_2$ were analyzed by the pseudo-first-order kinetics for the dimerization of **MeOSt**$^{\bullet+}$ with **MeOSt** and bimolecular reaction of **MeOSt**$^{\bullet+}$ with O$_2$ at the rate constant of approximately 10^7 M^{-1} s^{-1}.[9] In contrast to **MeOSt**$^{\bullet+}$, no effect of O$_2$ was observed for the formation and decay profiles of the transient absorption of other **S**$^{\bullet+}$.

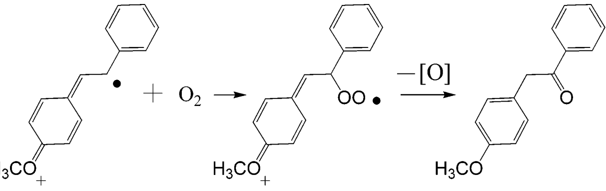
Discussion

Important Factors of the TPI Efficiency. Formation of **S**$^{\bullet+}$ was observed during the TPI of **S** bearing an electron-donating (methyl or methoxy) or an electron-withdrawing (chloro or cyano) substituent. According to the two-step two-photon absorption during the TPI, **S** is excited to **S** in the lowest excited singlet state (**S**(S$_1$)) by the first photon excitation at 308 nm, and **S**(S$_1$) is then excited to **S**(S$_n$) by the second photon excitation at 308 nm within 25-ns duration of the XeCl excimer laser flash. Since the energy of **S**(S$_n$) is higher than the IP of **S**, electron detachment from **S**(S$_n$) occurs to give **S**$^{\bullet+}$ and an electron, competitively with the internal conversion to **S**(S$_1$). The transient absorption of **S**$^{\bullet+}$ with a maximum peak at 470−490 nm increased with increasing F. Φ_{ion} was proportional to F^2, and slopes of the linear log−log plots of concentration of **S**$^{\bullet+}$ generated initially against F were approximately 2 as shown in Table 1. This relation is usually observed for the stepwise excitation mechanism of the TPI because two-photon absorption is necessary for ionization of **S** to give **S**$^{\bullet+}$.

Relationships between Φ_{ion} and E^{ox} of **S** or τ_f of **S**(S$_1$) have been reported for various substituted *trans*-stilbenes.[26] The dependence of Φ_{ion} on E^{ox} can be explained by the excess energy of **S**(S$_n$), which decreases with increasing IP. Because the relatively large [**S**$^{\bullet+}$] was observed for **S** with long τ_f, Φ_{ion} increases with increasing τ_f, except for **MeOSt** in air-saturated solution. In other words, Φ_{ion} depends on E^{ox} and τ_f, except for **MeOSt** in air-saturated AN solution.

Effects of O$_2$ Concentration on the TPI of MeOSt. To explain the exceptional behavior of **MeOSt** in air-saturated solution during the TPI of **S**, the following should be addressed. First, properties of **MeOSt**(S$_1$) generated from the first one-photon excitation may be different from those of other **S**(S$_1$). However, the absorption and emission spectra of **S** and τ_f of all **S**(S$_1$) resembled each other; therefore, **MeOSt**(S$_1$) has properties similar to those of other **S**. On the other hand, the absorption spectrum of **MeOSt**$^{\bullet+}$ was different from those of other **S**$^{\bullet+}$. It has been suggested that **MeOSt**$^{\bullet+}$ has the distonic character separation and localization of the positive charge on the oxygen of the *p*-methoxyl group and an unpaired electron on the β-olefinic carbon.[9] Because of the localization of an unpaired electron on the β-olefinic carbon, **MeOSt**$^{\bullet+}$ must have high reactivity against O$_2$. The distonic character is probably responsible to the different absorption spectrum of **MeOSt**$^{\bullet+}$ compared with other **S**$^{\bullet+}$.

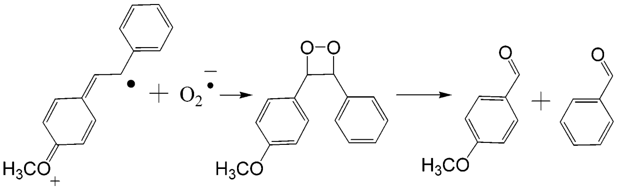
Next, we examined the TPI of **S** with the 355-nm 5-ns laser flash photolysis in Ar-, air-, and O$_2$-saturated AN to determine the concentration of **S**$^{\bullet+}$ immediately after the laser flash during the TPI of **S** (Figure 4). The concentration of **MeOSt**$^{\bullet+}$ immediately after the laser flash and the decay profile depended on the concentration of O$_2$. Although **S**$^{\bullet+}$ has no or less reactivity to O$_2$, **MeOSt**$^{\bullet+}$ reacts with O$_2$ at the rate constant of k_{O2} = $(0.9-1.4) \times 10^7$ M^{-1} s^{-1}(eq 2).[9]



(2)

Because of the distonic character of **MeOSt**$^{\bullet+}$, radical addition of O$_2$ to the β-olefinic carbon of **MeOSt**$^{\bullet+}$ occurs to give peroxy adduct ((**MeOSt**-O_2)$^{\bullet+}$), which leads to (4-methoxylphenyl)methyl phenyl ketone as a stable product. Since the concentrations of O_2 in air- and O_2-saturated AN are 2 and 9 mM, respectively, **MeOSt**$^{\bullet+}$ generated immediately after the laser flash cannot be bimolecularly quenched by O_2.

It has been reported that **MeOSt**$^{\bullet+}$ reacts with $O_2^{\bullet-}$ at almost diffusion-controlled rate (eq 3)[9,10,12] to give a dioxetane as the initial adduct which decomposes into 4-methoxylbenzaldehyde and benzaldehyde at room temperature. If $O_2^{\bullet-}$ is generated from the electron capture by O_2 during the TPI of **MeOSt** in the presence of O_2, $O_2^{\bullet-}$ may react with **MeOSt**$^{\bullet+}$. However, the concentration of $O_2^{\bullet-}$ was less than 10^{-6} M. Therefore, the quenching of **MeOSt**$^{\bullet+}$ cannot be explained by the bimolecular collisional reaction between **MeOSt**$^{\bullet+}$ and $O_2^{\bullet-}$. Consequently, the decay must correspond to a much faster reaction such as an intramolecular reaction or neutralization.



(3)

Ground-State Complex between MeOSt and O₂. It is suggested that a ground-state complex between **MeOSt** and O_2 (**MeOSt/**O_2) may play a key roll for the transient behavior of **MeOSt**$^{\bullet+}$ in the presence of O_2. When a apart of **MeOSt** forms the ground-state complex with O_2 in air- or O_2-saturated AN, reactions of **MeOSt**$^{\bullet+}$ and O_2 or $O_2^{\bullet-}$ in complex occur much faster than the bimolecular reaction rate, explaining the efficient quenching of **MeOSt**$^{\bullet+}$ by O_2 or $O_2^{\bullet-}$ (eqs 4 and 5).

$$\mathbf{MeOSt} + O_2 \rightleftarrows \mathbf{MeOSt/}O_2 \tag{4}$$

$$\mathbf{MeOSt/}O_2 + 2h\nu\ (308\ \text{nm}) \rightarrow \mathbf{MeOSt}^{\bullet+}/O_2 + e^-, \mathbf{MeOSt}^{\bullet+}/O_2^{\bullet-} \tag{5}$$

Thus, the low Φ_{ion} value of **MeOSt**$^{\bullet+}$ during the TPI of **MeOSt** can be explained by the fast reaction between **MeOSt**$^{\bullet+}$ and O_2 or $O_2^{\bullet-}$ in the complex before dissociation to free **MeOSt**$^{\bullet+}$ and O_2 or $O_2^{\bullet-}$. The ground-state complexes with various compounds such as benzophenone[32] and cyclobutane-type *cis,syn*-dimer of dimethylthymine.[33] The complex formation of **MeOSt/**O_2 is supported by the fact that the fluorescence quantum yield of **MeOSt** in O_2-saturated AN (0.015) was lower than that in Ar-saturated AN (0.02). The deactivation pathway in **MeOSt**(S_1)**/**O_2 proceeds faster than that in free **MeOSt**(S_1). This may relate to the low Φ_{ion} value of **MeOSt**$^{\bullet+}$ in the presence of O_2.

Finally, it should be mentioned that Φ_{ion} of **S** depends not only on E^{ox} of **S** and τ_f of **S**(S_1) but also ground-state complex formation between **MeOSt** with O_2 and reactivity of **MeOSt**$^{\bullet+}$ during the TPI of **S** using lasers having a long duration such as excimer lasers. The decay of **MeOSt**$^{\bullet+}$ corresponds to bimolecular reactions such as addition reactions between **MeOSt**$^{\bullet+}$ and O_2 or $O_2^{\bullet-}$ (eqs 2 and 3, neutralization of **MeOSt**$^{\bullet+}$ with $AN^{\bullet-}$ and $(AN)_2^{\bullet-}$, and dimerization of **MeOSt**$^{\bullet+}$ with **MeOSt**. Thererfore, it is clear that the concentration of **MeOSt**$^{\bullet+}$ depends on the time when **MeOSt**$^{\bullet+}$ is monitored after the laser flash.

In the previous paper we reported that radical cations of **St** and **MeOSt** generated oxidized products in high yields (64 and 68%, respectively) in O_2-saturated AN. From the present results, TPI yield of **MeOSt** is much smaller than St. Thus, the complex MeOSt with O_2 generated oxidized product efficiently with a laser pulse duration, while **St**$^{\bullet+}$ forms the oxidized products with bimolecular manner.

Conclusions

S$^{\bullet+}$ was generated from the TPI of **S** in AN with irradiation of a XeCl laser flash with high F. Φ_{ion} was proportional to F^2. Linear relationships between Φ_{ion} (0.06−0.29) and E^{ox} of **S** and τ_f were observed, except for **MeOSt.** The TPI proceeds via the two-step two-photon excitation of the **S**(S_0) → **S**(S_1) → **S**(S_n) transition, and ionization from **S**(S_n) to give **S**$^{\bullet+}$ and electron. It is found that Φ_{ion} of **S**$^{\bullet+}$ during the TPI depends not only on E^{ox} of **S** and τ_f of **S**(S_1), except for **MeOSt**$^{\bullet+}$, but also on the time for the detection of **MeOSt**$^{\bullet+}$ after the laser flash. It is suggested that the ground-state complex between **MeOSt** and O_2 and the distonic character of **MeOSt**$^{\bullet+}$ with separation and localization of the positive charge on the oxygen of the *p*-methoxyl group and an unpaired electron on the β-olefinic carbon, are responsible to the fast reaction of **MeOSt**$^{\bullet+}$ with O_2 or $O_2^{\bullet-}$, leading to the considerable low yield and fast decay of **MeOSt**$^{\bullet+}$.

Acknowledgment. This work has been partly supported by a Grant-in-Aid for Scientific Research on Priority Area (417), 21st Century COE Research, and others from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

JO050317N

---

(32) Hutchinson, J. A.; DiBenedetto, J.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 6517.

(33) Majima, T.; Pac, C.; Kubo, J.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 377.