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Citation	Radiation Physics and Chemistry, 75(2), 195-200 https://doi.org/10.1016/j.radphyschem.2005.08.016
Issue Date	2006-02
Doc URL	https://hdl.handle.net/2115/15414
Type	journal article
File Information	RPC75-2.pdf



Solvent Effects on the Photochemistry of Dimethyl Sulfoxide–Cl Complexes
Studied by Combined Pulse Radiolysis and Laser Flash Photolysis

[Photochemistry of DMSO–Cl complexes]

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Abstract

Photolysis of complexes of dimethyl sulfoxide (DMSO) with chlorine atoms results in rapid and permanent photobleaching which may be due to intramolecular hydrogen abstraction. The effects of solvent polarity were examined in a wide variety of DMSO-carbon tetrachloride mixed solvents. The quantum yields of photobleaching decreased from 0.27 to 0.08 as the solvent polarity increased, while significant changes were observed in the low DMSO concentration range ($< 0.2 \text{ mol dm}^{-3}$). This cannot be accounted for by simple solvent polarity effects. The effects of polar and nonpolar additives were also examined and it is concluded that the specific solvation effect of DMSO was the main cause of the significant change in the quantum yields in the low concentration range of DMSO.

Keywords: DMSO–Cl complex; Pulse radiolysis; Photochemistry; Intramolecular hydrogen abstraction; Solvation effect

1. Introduction

Direct kinetic measurements of the reactivities of free chlorine atoms (Sumiyoshi and Katayama, 1990a) and various chlorine atom complexes with benzene (Sumiyoshi, 1997) and carbon disulfide (CS_2) (Sumiyoshi et al., 2005a) toward alcohols have been carried out to elucidate the increased selectivity of the tertiary to primary hydrogen abstraction of the chlorine atom complexes. These chlorine atom complexes have lower reactivities and

higher selectivities than those of free chlorine atoms (Sumiyoshi et al., 2005a). On the other hand, DMSO–Cl complexes are much less reactive toward alcohols (Sumiyoshi and Katayama, 1990a). Therefore, DMSO–Cl complexes have become known as an excellent reference system for competition reactions of free chlorine atoms, due to their easily detectable absorption band ($\lambda_{\text{max}} = 400 \text{ nm}$) (Sumiyoshi and Katayama, 1987) and the stable nature (Sumiyoshi and Katayama, 1990a; Sumiyoshi et al., 1987). Radiolysis of dimethyl sulfoxide (DMSO) in carbon tetrachloride (CCl_4) (Sumiyoshi and Katayama, 1987) and CCl_4 in DMSO (Sumiyoshi and Katayama, 1990b) results in the formation of transient DMSO–Cl complexes with an absorption maximum at 400 nm. Since DMSO is a polar aprotic solvent with a relatively large dipole moment and CCl_4 is a nonpolar liquid, a wide range of polarities can be applied to solvents by using mixtures of DMSO– CCl_4 . These results make DMSO– CCl_4 mixed solvents suitable for producing DMSO–Cl complexes and for studying the effect of solvent polarity on their reactions.

Photochemical studies of benzene–Cl π -complexes (Wu et al., 1996, 1997) and CS_2 –Cl σ -complexes (Sumiyoshi et al., 2005b) have shown that the reactivity of excited CS_2 –Cl complexes is much higher than that of excited benzene–Cl and substituted benzene–Cl complexes, opposite to the reactivities of their ground states, where the reactivity of CS_2 –Cl complexes is much lower than that of benzene–Cl complexes (Sumiyoshi et al., 2005a). Since DMSO–Cl complexes are the much less reactive (Sumiyoshi and Katayama, 1990a; Kumar and Neta, 1992) among these chlorine atom complexes, a much higher reactivity in photolysis can be expected. A combined pulse radiolysis-flash

photolysis technique is a convenient method to investigate photochemical reactions of short-lived species, because the first radiation pulses do not interact with the transient species (Bromberg et al., 1985; Ebbesen, 1988). Applying this technique to halocarbon solutions, some chlorine atom π -complexes with diphenyl sulfide (DPS) (Sumiyoshi et al., 1992, 1993), and arenes (Wu et al., 1996, 1997) have been characterized. The reaction mode was found to depend on the bond dissociation energy of related molecules. Recently, preliminary photochemical studies of DMSO–Cl complexes were carried out in DMSO/CCl₄ mixed solvents using a combined pulse radiolysis-laser flash photolysis technique, which found relatively high quantum yields (> 0.24) of photobleaching, may be due to intramolecular hydrogen abstraction and the significant solvent dependence of the quantum yields (Sumiyoshi et al., 2005c). In this work, photochemistry of DMSO–Cl complexes was investigated in DMSO/1,2-dichloroethane mixed solvents and different effects of the DMSO concentration on the photobleaching quantum yields from those observed in the DMSO/CCl₄ mixed solvents were found. The intramolecular hydrogen abstraction mechanism of the excited DMSO–Cl complexes in the DMSO/CCl₄ mixed solvents is discussed in detail based on effects of polar and nonpolar additives and the bond dissociation energies of the related molecules.

2. Experimental

2.1. Materials

Carbon tetrachloride, 1,2-dichloroethane, benzene (spectral grade), DMSO (dehydrated), naphthalene (scintillation grade), and benzophenone (special guaranteed

reagent grade) from Wako Junyaku were used as received. Dilute solutions in rectangular quartz cells were deaerated by bubbling argon and sealed with Teflon bulbs prior to irradiation. Argon of ultrahigh purity was obtained from Hoxan.

2.2 *Combined Pulse Radiolysis-Laser Flash Photolysis*

The DMSO–Cl complexes were produced by pulse radiolysis using 10–50 ns, 45 MeV electron pulses from an S-band linear accelerator (Mitsubishi) at Hokkaido University. For the laser flash photolysis studies of complexes, successive electron pulse irradiation and laser photolysis was carried out using a pulse radiolysis-laser flash photolysis system with a time resolution of 10 ns described elsewhere (Sumiyoshi et al., 1993). Due to the short optical path length (0.6 cm) of this system, 50 ns electron pulse and a dose up to 110 Gy was used. The laser photolysis was carried out from the opposite side of the electron beam with a third harmonic pulse (355 nm, 6 ns duration) from an Nd:YAG laser (Quanta-Ray, DCR-11). Dosimetry and actinometry have been described before (Sumiyoshi et al., 2005b). All experiments were carried out at room temperature (16 ± 2 °C). The experimental uncertainty is $\pm 10\%$ for the quantum yields of photobleaching.

3. Results and Discussion

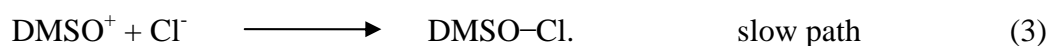
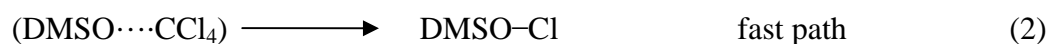
3.1. *Formation of DMSO–Cl Complexes*

The DMSO–Cl complexes ($\lambda_{\text{max}} = 400$ nm) were produced by irradiation of deaerated

DMSO-CCl₄ mixtures. Fig. 1 shows typical transient absorption spectra observed by pulse radiolysis in CCl₄ (Fig. 1a) and in DMSO (Fig. 1b). In CCl₄ and other halocarbons, the Cl atoms initially produced react with DMSO to yield DMSO-Cl complexes (Sumiyoshi and Katayama, 1987; Alfassi et al., 1989):



The complexes are formed via two different paths in DMSO, reactions (2) and (3), and the contributions of the two paths have been shown to depend on the CCl₄ concentration (Sumiyoshi and Katayama, 1990b):

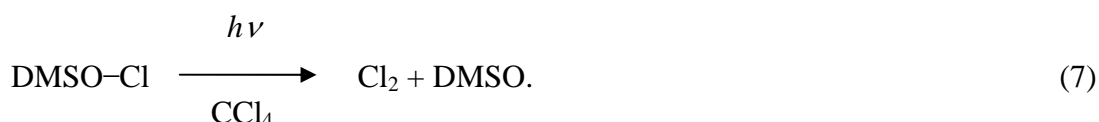


The slow formation path (3) is dominant at CCl₄ concentrations below 10⁻² mol dm⁻³; higher CCl₄ concentrations make the fast path (2) more dominant. The fast formation of DMSO-Cl complexes has been shown to proceed by direct excitation of preassociated (DMSO⋯CCl₄) pairs, based on laser flash photolysis experiments (Sumiyoshi et al., 1990). The slow path has been ascribed to the reaction of DMSO⁺ and Cl⁻ based on the results of pulse radiolysis experiments of alkaline chlorides in DMSO. The latter path has been demonstrated in acidic aqueous solutions as well (Kishore and Asmus, 1991). The extinction coefficient at the absorption maximum of DMSO-Cl complexes in CCl₄ was determined using the radiation chemical yield of the chlorine atoms in CCl₄ of 0.17 μmol J⁻¹ as reported previously (Sumiyoshi et al., 1993). The obtained extinction coefficient value of 7800 ± 50 dm³ mol⁻¹ cm⁻¹ at 400 nm was applied to DMSO-CCl₄ mixtures, while the extinction coefficients at other wavelengths were determined based on the spectrum

obtained with each mixture.

3.2. Photochemistry of DMSO–CCl₄ Complexes

Fig. 2 shows kinetic traces observed at 400 nm by combined pulse radiolysis-laser flash photolysis of DMSO/CCl₄ mixtures (1/100, 1/1, and 9/1 volume ratio). Laser flash photolysis resulted in rapid and permanent photobleaching of DMSO–Cl complexes indicating short lifetimes (< 10 ns) of the excited DMSO–Cl complexes. The quantum yields of photobleaching were calculated to be 0.21, 0.13, and 0.065 for 1/100, 1/1, and 9/1 (v/v) DMSO/CCl₄ mixtures respectively. Rapid and permanent photobleaching was also observed at irradiation of DMSO containing 8.5×10^{-4} mol dm⁻³ KCl (Fig. 3). The following intramolecular and intermolecular photoreactions may be expected for the excited DMSO–Cl complexes:



Theoretical calculations gave bond dissociation enthalpy values of 431 kJ mol⁻¹ for Cl–H and 412 for CH₃S(O)CH₂–H (Sayin and McKee, 2004), indicating that the Cl atom

can abstract a hydrogen atom exothermically (-19 kJ mol^{-1}) from DMSO, reactions (4) and (6). However, the photobleaching quantum yield decreases as the DMSO concentration increases, reaction (6) cannot account for the photobleaching. The DMSO^+ ions produced by reaction (5) should react with solute Cl^- ions in DMSO containing KCl leading to the rapid recovery of the photobleaching. However, the experimental results showed only the permanent photobleaching as shown in Fig. 3. Considering the bond dissociation energies of $\text{Cl}-\text{Cl}$ ($242.58 \text{ kJ mol}^{-1}$) and $\text{Cl}-\text{CCl}_3$ (305.9) (Lide, 1995), reaction (7) is endothermic (63.3 kJ mol^{-1}). Consequently, the observed photobleaching could be assigned to the intramolecular hydrogen abstraction (reaction (4)) as observed for methyl-substituted benzenes-Cl complexes (Wu et al., 1997; Sumiyoshi et al., 1992).

3.3. *Effects of Additives*

The effects of polar and nonpolar additives were examined. Fig. 4 shows the kinetic traces observed by pulse radiolysis-laser flash photolysis of $1.1 \times 10^{-2} \text{ mol dm}^{-3}$ DMSO in CCl_4 in the presence of 1-propanol. At 1-propanol ($\mu = 3.09 \text{ D}$) concentrations of 1.7×10^{-2} to $6.7 \times 10^{-2} \text{ mol dm}^{-3}$, a constant value of the photobleaching quantum yield ($\Phi = 0.36 \pm 0.01$) was obtained (Table 1). This value is much higher than that obtained in the absence of 1-propanol ($\Phi = 0.24$), suggesting the reaction between excited $\text{DMSO}-\text{Cl}$ complexes and 1-propanol. However, the concentration independent quantum yields strongly indicate the absence of intermolecular reactions between excited $\text{DMSO}-\text{Cl}$ complexes and 1-propanol. The effects of 1-propanol may be ascribed to the suppression of the specific solvation effect discussed later. The effects of nonpolar benzene is also

given in Table 1. Different from 1-propanol, benzene exerts no influence on the quantum yield at concentrations up to $1.1 \times 10^{-1} \text{ mol dm}^{-3}$.

3.4. *Effects of Solvents*

The effects of solvent polarity was examined. The quantum yields of photobleaching in nonpolar CCl_4 and in polar 1,2-dichloroethane ($\mu = 1.86 \text{ D}$) are compared in Table 2. The same photobleaching quantum yield ($\Phi=0.26$) was obtained at $[\text{DMSO}] = 1.4 \times 10^{-2} \text{ mol dm}^{-3}$ in both solvents, while a lower quantum value ($\Phi=0.16$) was obtained at $[\text{DMSO}] = 2.8 \times 10^{-1} \text{ mol dm}^{-3}$ in CCl_4 , indicating the effect of solute DMSO ($\mu = 3.9 \text{ D}$).

Fig. 5 shows the quantum yields of photobleaching obtained for DMSO/ CCl_4 mixtures as a function of the mole fraction of DMSO. The quantum yield of 0.093 obtained with $2 \times 10^{-2} \text{ mol dm}^{-3}$ KCl in DMSO is also plotted for neat DMSO (14.1 mol dm^{-3}). As the dilute DMSO solution gave the highest quantum yield, the effects of DMSO in the concentration range 10^{-3} – $2 \times 10^{-1} \text{ mol dm}^{-3}$ were investigated in detail and are given in Fig. 6. The photobleaching quantum yield decreases from 0.27 to 0.08 with DMSO concentration increases as shown in Figs. 5 and 6. This result may be evidence of the effects of increasing solvent polarity with increasing DMSO concentration (Prestbo and McHale, 1984). However, the significant decrease at low $[\text{DMSO}] (<0.1 \text{ mol dm}^{-3})$ cannot be accounted for by solvent polarity effects. DMSO is in the highly associated molecule category due to the anomalous concentration dependence of some of the physical properties of DMSO in various solvents (Szmant, 1971). The formation of a cyclic dimer has been suggested on the basis of infrared studies of DMSO in CCl_4 (Figuroa et al.,

1966; Prestbo et al., 1983). Spectroscopic as well as thermodynamic (Prestbo and McHale, 1984; Griggs et al., 1979; Chareyron and Clechet, 1971; Agarwal et al., 1979; Quitzsch et al., 1967) and nuclear magnetic relaxation (Sayin and McKee, 2004) data support the formation of DMSO dimers at low concentrations. The DMSO dimer seems to predominate in the concentration range $0.02\text{--}0.3\text{ mol dm}^{-3}$, and the value of its formation constant is estimated as $0.9\text{ dm}^3\text{ mol}^{-1}$ (Figueroa et al., 1966). Thus, DMSO monomers exist predominantly in the concentration range below $8 \times 10^{-3}\text{ mol dm}^{-3}$, and the significant decrease of the quantum yield at low [DMSO] may be induced by the association of DMSO. Previous pulse radiolysis experiments suggest a significant contribution of the ionic form $\text{DMSO}^+\text{--Cl}^-$ for DMSO–Cl complexes (Sumiyoshi and Katayama, 1990b; Kumar and Neta, 1992). Much larger contributions of the ionic form for the excited DMSO–Cl complexes could be expected. Since DMSO is known as a good solvator for cations (Hammett, 1970), efficient stabilization of the excited complexes could lead to the decrease in the quantum yield.

Similar strong solvent effects on the rate constants have been reported for the reactions of ground state DMSO–Cl complexes with various compounds in DMSO/ CH_2Cl_2 and DMSO/water solvents (Kumar and Neta, 1992). These effects have been ascribed to be partly due to the solvent polarity, but are mainly due to the specific solvation effect described above.

4. Conclusion

Photolysis of DMSO–Cl complexes produced in the DMSO/CCl₄ mixed solvent resulted in rapid and irreversible photobleaching due to intramolecular hydrogen abstraction. The quantum yields of the photobleaching decreased with increasing solvent polarity as the DMSO concentration increased. However, significant effects were observed at low DMSO concentration and these may be ascribed to the specific solvation effect of DMSO. The effects of polar and nonpolar additives also support the above conclusion.

Acknowledgements

The authors are grateful to Messrs. Hiroaki Tanida and Koichi Sato for their help in operating the linear accelerator.

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Figure Captions

Fig. 1. Transient absorption spectra of DMSO–Cl complexes observed in pulse radiolysis: (a) argon saturated $1.1 \times 10^{-2} \text{ mol dm}^{-3}$ DMSO in CCl_4 , immediately after the pulse, absorbed dose 100 Gy/pulse; (b) argon saturated $6.5 \times 10^{-3} \text{ mol dm}^{-3}$ CCl_4 in DMSO, $8 \mu\text{s}$ after the pulse, absorbed dose 118 Gy/pulse.

Fig. 2. Kinetic traces observed at 400 nm by pulse radiolysis-laser flash photolysis (355 nm) of argon saturated (a) 1/100, (b) 1/1, and (c) 9/1 (v/v) DMSO/ CCl_4 mixtures. Absorbed dose 104 Gy/pulse.

Fig. 3. A kinetic trace observed by pulse radiolysis-laser flash photolysis of argon saturated $8.5 \times 10^{-4} \text{ mol dm}^{-3}$ KCl in DMSO. Absorbed dose 100Gy/pulse.

Fig. 4. Kinetic traces observed at 400 nm by pulse radiolysis-laser flash photolysis (355 nm) of $1.1 \times 10^{-2} \text{ mol dm}^{-3}$ DMSO in CCl_4 in the presence of 1-propanol. [1-propanol]: (a) 1.7×10^{-2} ; (b) 3.4×10^{-2} ; (c) $6.7 \times 10^{-2} \text{ mol dm}^{-3}$.

Fig. 5. Quantum yields of photobleaching of DMSO–Cl complexes in DMSO/ CCl_4 mixed solvents versus the mole fraction of DMSO.

Fig. 6. Quantum yields of photobleaching of DMSO–Cl complexes in CCl_4 versus DMSO concentration.

Table 1. Effects of Additives on the Quantum Yields of Photobleaching of DMSO-Cl Complexes in $1.1 \times 10^{-2} \text{ mol dm}^{-3}$ DMSO in CCl_4

additive	[additive]/ mol dm^{-3}	$\Phi(\text{photobleach})$
none	-	0.24 ± 0.02
1-propanol	1.7×10^{-2}	0.35 ± 0.02
1-propanol	3.4×10^{-2}	0.35 ± 0.02
1-propanol	6.7×10^{-2}	0.37 ± 0.02
benzene	1.1×10^{-1}	0.24 ± 0.02

Table 2. Effects of Solvents on the Quantum Yields of Photobleaching of DMSO-Cl Complexes

[DMSO] / mol dm ⁻³	solvent	Φ(photobleach)
1.4 × 10 ⁻²	CCl ₄	0.26 ± 0.02
1.4 × 10 ⁻²	1,2-DCE	0.26 ± 0.02
2.8 × 10 ⁻¹	CCl ₄	0.16 ± 0.01
2.8 × 10 ⁻¹	1,2-DCE	0.23 ± 0.02

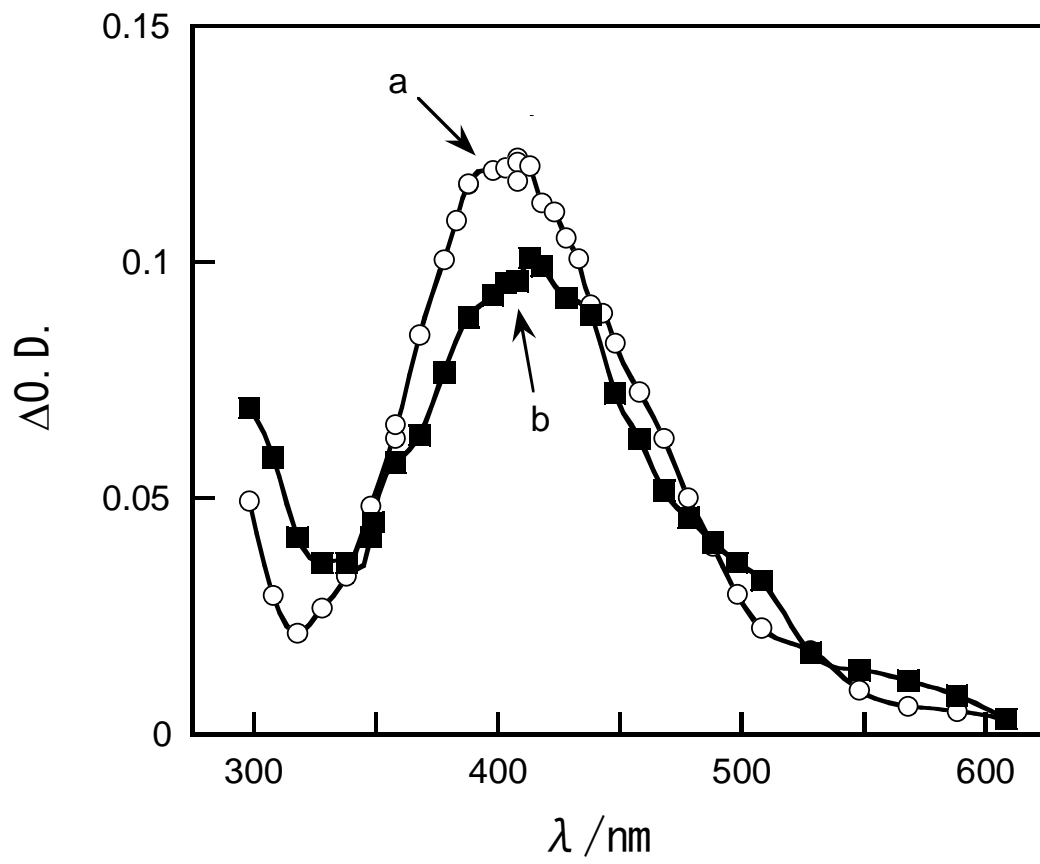


Fig. 1 Sumiyoshi et al

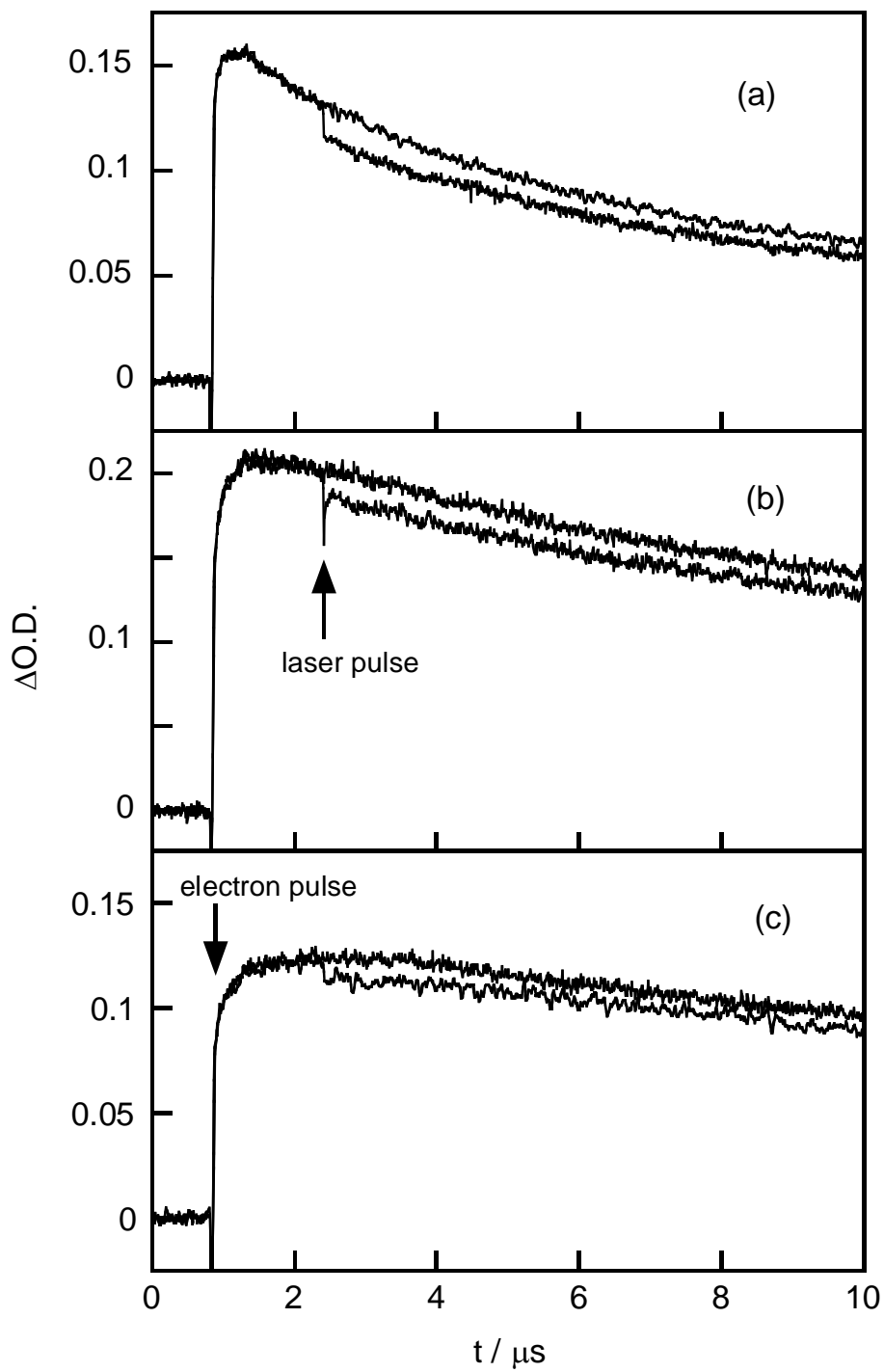


Fig. 2 Sumiyoshi et al

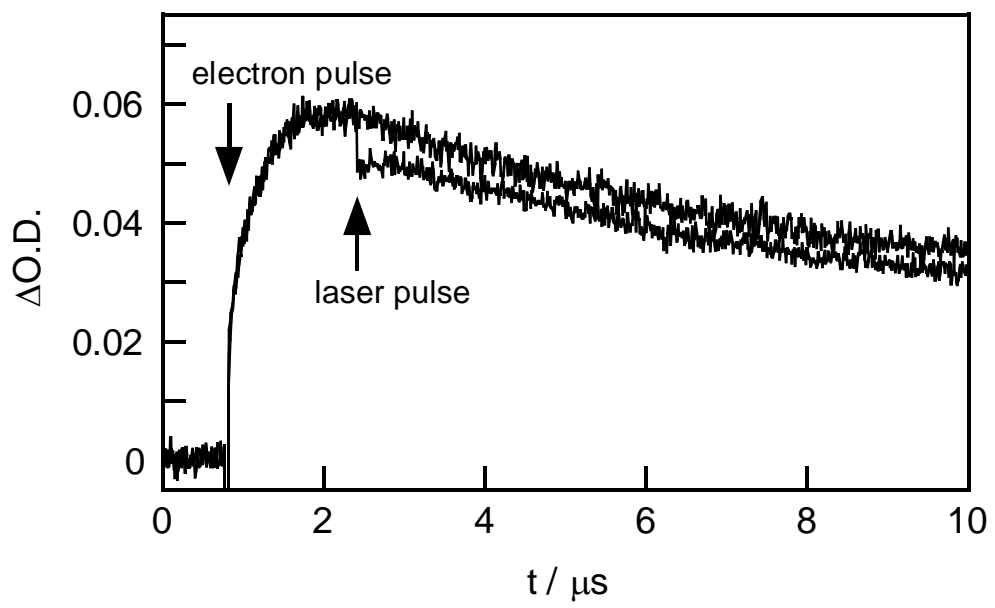


Fig. 3 Sumiyoshi et al

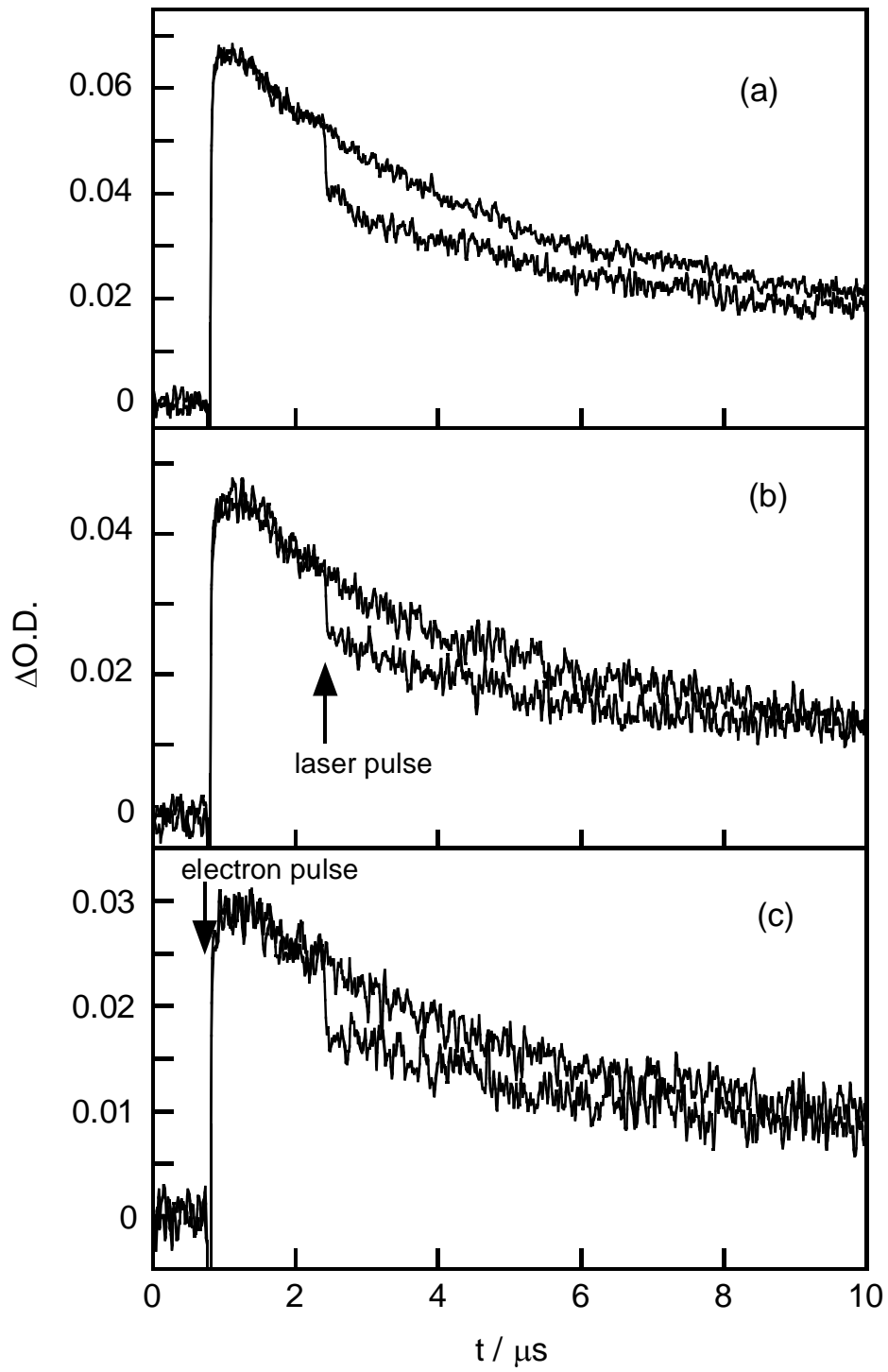


Fig. 4 Sumiyoshi et al

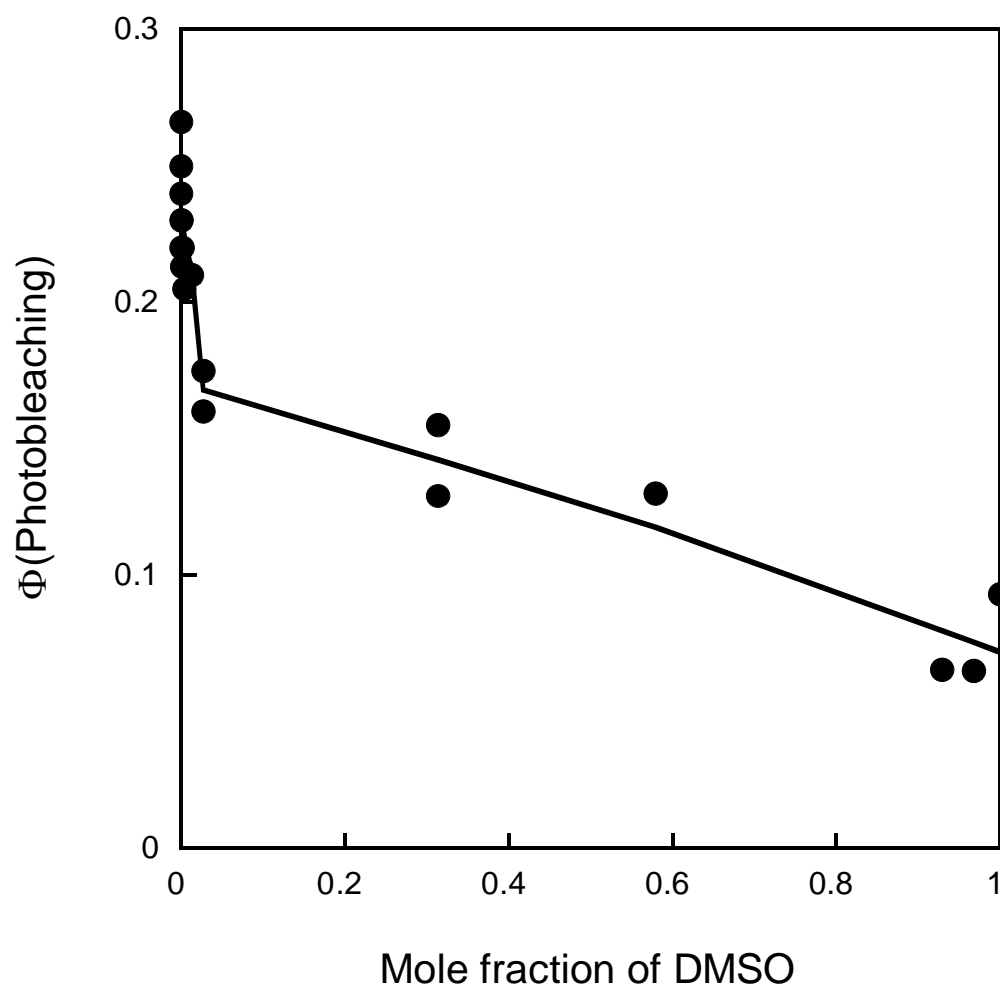


Fig. 5 Sumiyoshi et al

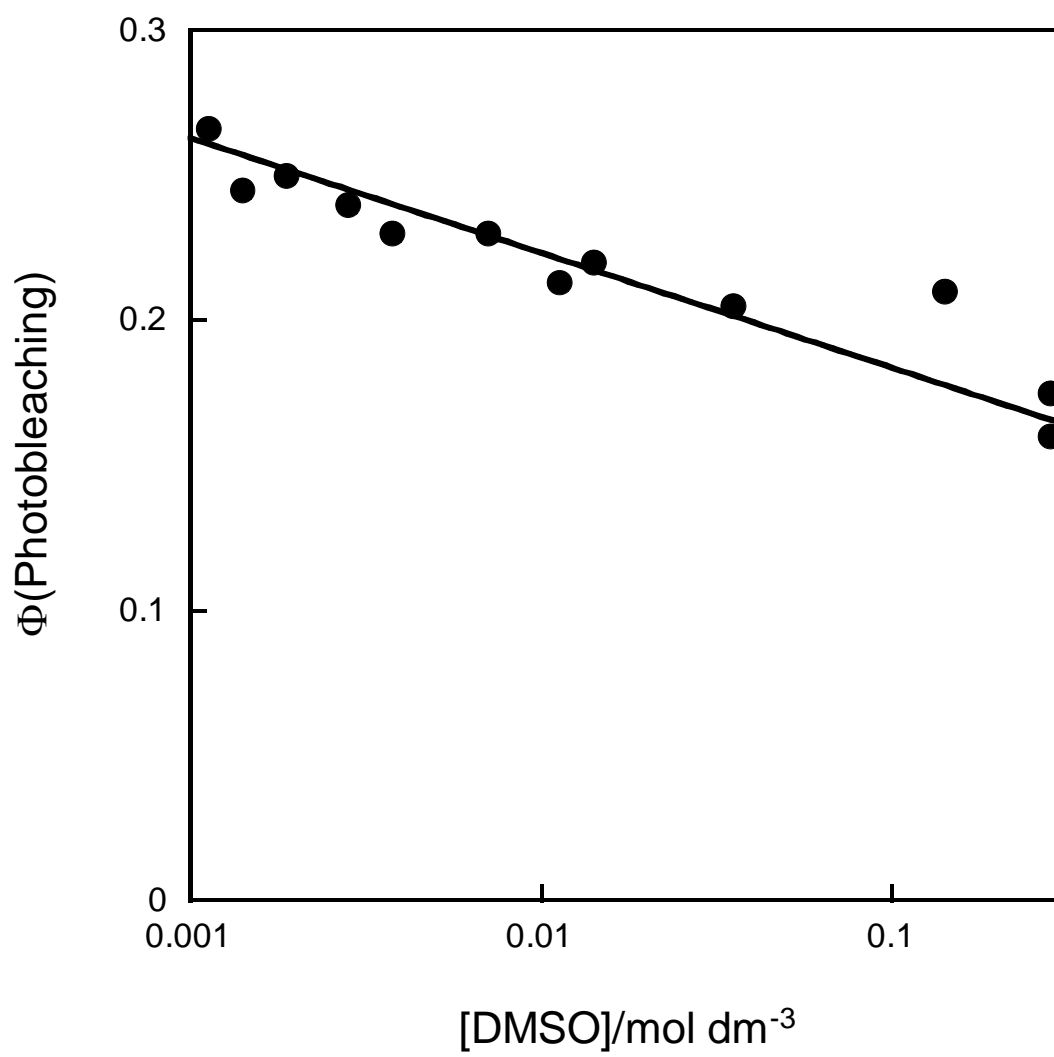


Fig. 6 Sumiyoshi et al