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Author(s)	Okubo, Yu; Kido, Yuta; Fujiyoshi, Ryoko et al.
Citation	Radiation Physics and Chemistry, 78(12), 1161-1163 https://doi.org/10.1016/j.radphyschem.2009.07.005
Issue Date	2009-12
Doc URL	https://hdl.handle.net/2115/45296
Type	journal article
File Information	sumiyoshi_RPC78.pdf



Formation and Photochemistry of Organic Sulfur Compound–Chlorine Atom Complexes

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Abstract

Photochemical reactions of organic sulfur compounds (CH_3SCH_3 , $\text{C}_2\text{H}_5\text{SCH}_3$, and $\text{C}_2\text{H}_5\text{SC}_2\text{H}_5$)–chlorine atom complexes have been studied using a combined pulse radiolysis–laser flash photolysis technique. Excitation of all complexes has resulted in photobleaching with a similar quantum yield (0.37 ± 0.07), independent of solvent polarities and concentration of solutes. The results were compared with previous studies of the analogous dimethyl sulfoxide (DMSO)–Cl complexes. It is concluded that the significant change of photobleaching quantum yields of the excited DMSO–Cl complex observed in the DMSO– CCl_4 mixed solvent is mainly due to the specific solvation effect of DMSO for cations.

Keywords: Organic sulfur–Cl complex; Pulse radiolysis; Laser flash photolysis; Specific solvation

1. Introduction

Photochemical studies of dimethyl sulfoxide–chlorine atom complexes (DMSO–Cl) produced in DMSO/CCl₄ mixed solvents have shown that the photolysis of the complex results in rapid and irreversible photobleaching due to intramolecular hydrogen abstraction (Sumiyoshi et al., 2006a). The quantum yields of the photobleaching decreased with increasing solvent polarity as the DMSO concentration increased. However, significant changes were observed at low DMSO concentration (<0.2 mol dm⁻³), which is supposed to be due to the specific solvation effect of DMSO for cations. The effects of polar and nonpolar additives also supported the above conclusion.

In this study, the photochemistry of chlorine atom complexes of organic sulfur compounds such as dimethyl sulfide (CH₃SCH₃, DMS), ethyl methyl sulfide (C₂H₅SCH₃, EMS), and diethyl sulfide (C₂H₅SC₂H₅, DES) which do not possess specific solvation characteristics, is investigated in order to elucidate the importance of the specific solvation effect of DMSO. The effects of solvent polarity and concentrations of solutes on quantum yields of photobleaching are observed and discussed.

2. Experimental

2.1. Combined pulse radiolysis-laser flash photolysis

The organic sulfur compound–Cl complexes were produced by pulse radiolysis using 10 ns, 45 MeV electron pulses from an S-band linear accelerator (Mitsubishi) at Hokkaido University. For laser flash photolysis studies of complexes, successive electron pulse irradiation and laser photolysis were carried out using a pulse radiolysis-laser flash photolysis system. Because of the short optical path length (0.6 cm) of this system, 50 ns electron pulses were used. The laser flash photolysis was conducted with a third harmonic pulse (355 nm, 6 ns width) from an Nd:YAG laser (Quanta-Ray, DCR-11). Dosimetry and actinometry have been described in elsewhere (Sumiyoshi et al., 2006b). All experiments were carried out at room temperature (16 ± 2°C). The experimental uncertainty is estimated to be ±10% for the quantum yields of photobleaching.

2.2. Materials

Carbon tetrachloride, 1, 2-dichloroethane (1,2-DCE), benzene (spectral grade), DMS (98.0%), DES (97.0%), naphthalene (scintillation grade), and benzophenone (spectral–guaranteed reagent grade) from Wako Junyaku, and EMS (96%) from Aldrich were used as received. Samples were irradiated after bubbling with argon in a

rectangular quartz cell sealed with a Teflon bulb. Argon (ultra-high purity) was obtained from Hoxan.

3. Results and discussion

3.1. Formation of sulfur compounds–Cl complexes

Fig. 1 shows transient absorption spectra observed after pulse radiolysis of DMS, EMS and DES in CCl₄. DMS–Cl, EMS–Cl, and DES–Cl complexes were formed from the reaction of Cl atoms, and these transients exhibited absorption maxima around 350 nm, 50 nm blue-shifted from that of DMSO–Cl. The value of λ_{max} for DMS–Cl complexes was identical with those reported previously (Urbanski and Wine, 1999; Chaundhi et al., 1984; Bonifačić and Asmus, 1980). The extinction coefficients at the absorption maximum of these complexes in CCl₄ were determined using the radiation chemical yield of chlorine atoms in CCl₄ of 0.17 $\mu\text{mol J}^{-1}$ (Sumiyoshi et al., 1993), and are listed in Table 1.

3.2. Photochemistry of sulfur compounds–Cl complexes

Upon laser flash photolysis of the complexes, photobleaching was observed for all excited complexes. Fig.2 shows typical kinetic traces recorded at the absorption maximum wavelength by combined pulse radiolysis-laser flash photolysis of DMS, EMS, and DES in CCl₄. Photobleaching was also observed after radiolysis and photolysis of sulfur compounds in 1,2-dichloroethane (1,2-DCE). These permanent photobleaching can be assigned to the intramolecular hydrogen abstraction as observed for DMSO–Cl complexes (Sumiyoshi et al., 2006a).

3.3. Effects of solvent polarity

The effects of solvent polarity on quantum yields of photobleaching were examined. The quantum yields of photobleaching were calculated for DMS–Cl, EMS–Cl, and DES–Cl complexes in nonpolar CCl₄ and polar 1,2-DCE mixed solvents. Polarity of the solvent was adjusted by changing the volume ratio of CCl₄/1,2-DCE mixture. Fig. 3 shows the quantum yields of photobleaching obtained for DMS–Cl and DES–Cl complexes as a function of mole fraction of 1,2-DCE in CCl₄/1,2-DCE mixed solvents. The quantum yields were found to be constant as 0.37 ± 0.05 , independent of sulfur compounds and solvent polarity. These results strongly indicate that the solvent polarity does not affect the quantum yields of photobleaching in the photolysis of complexes under investigation.

3.4. Effects of concentrations of sulfur compounds

The effects of concentrations of sulfur compounds on photobleaching quantum yields were also examined. The results observed in the concentration range from 2.5×10^{-3} to 4.8×10^{-2} mol dm⁻³ are shown in Fig. 4. The photobleaching quantum yields were independent of sulfur compounds and their concentrations and estimated as 0.37 ± 0.07 . In the case of DMSO–Cl complexes, the photobleaching quantum yield decreased from 0.27 to 0.18 with DMSO concentration increased from 1.0×10^{-3} to 2.0×10^{-1} mol dm⁻³ (Sumiyoshi, 2006a). Previous studies have suggested a significant contribution of the partial ionic form DMSO^{δ+}–Cl^{δ-} for the ground state DMSO–Cl complexes (Sumiyoshi and Katayama, 1990; Kumar and Neta, 1992). Thus, the larger contributions of the ionic form for excited DMSO–Cl complexes than that of ground state can be expected. Additionally, DMSO is known as a good cation solvator (Hammett, 1970). It seems that free DMSO forms the solvation shell around excited DMSO–Cl complexes. The solvation shell might stabilize the excited complexes resulting in a decrease of the quantum yield. Since such solvation effects can not be expected for the sulfur compounds under investigation, photolysis of DMS–Cl, EMS–Cl, and DES–Cl complexes exhibit a constant quantum yield value ($\Phi = 0.37$), much higher than those of DMSO–Cl complexes ($\Phi = 0.08$ – 0.27). It should be noted that higher values of quantum yields ($\Phi = 0.36 \pm 0.01$) of photobleaching of DMSO–Cl complexes have also been observed by adding small amount of 1-propanol (1.7 – 6.7×10^{-2} mol dm⁻³) expected to suppress the specific solvation effect of DMSO (Sumiyoshi et al., 2006a). The present results confirm that the significant change of photobleaching quantum yields observed for DMSO–Cl complexes is due to the specific cation solvation effect of DMSO.

Acknowledgements

The authors are grateful to Mr. Koichi Sato for his help in operating the linear accelerator.

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Figure legends

Fig. 1. Transient absorption spectra of DMS–Cl, EMS–Cl and DES–Cl complexes observed in pulse radiolysis: (a) argon saturated $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ DMS in CCl_4 , 2 μs after the pulse, absorbed dose $100 \text{ Gy pulse}^{-1}$; (b) argon saturated $2.9 \times 10^{-2} \text{ mol dm}^{-3}$ EMS in CCl_4 , 2 μs after the pulse, absorbed dose 92 Gy pulse^{-1} ; (c) argon saturated $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ DES in CCl_4 , 2 μs after the pulse, absorbed dose 87 Gy pulse^{-1} .

Fig. 2. Kinetic traces observed by pulse radiolysis-laser flash photolysis (355 nm) of argon saturated sulfur compounds in CCl_4 : (a) observed at 360 nm, $4.8 \times 10^{-3} \text{ mol dm}^{-3}$ DMS, absorbed dose 90 Gy pulse^{-1} ; (b) observed at 355 nm, $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ EMS, absorbed dose 95 Gy pulse^{-1} ; (c) observed at 370 nm, $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ DES, absorbed dose 95 Gy pulse^{-1} .

Fig. 3. Quantum yields of photobleaching of DMS–Cl and DES–Cl complexes in CCl_4 /1,2-DCE mixed solvents versus the mole fraction of 1,2-DCE. The dashed line indicates quantum yield value of 0.37.

Fig. 4. Quantum yields of photobleaching of DMS–Cl, EMS–Cl, and DES–Cl complexes in CCl_4 versus the concentrations of sulfur compounds. The dashed line indicates quantum yield value of 0.37.

Table 1. Absorption maxima and extinction coefficients of sulfur compound–Cl complexes

complexes	$\lambda_{\text{max}} / \text{nm}$	$\varepsilon / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$
DMS–Cl	360	6500 ± 300
EMS–Cl	355	7200 ± 200
DES–Cl	370	5200 ± 200

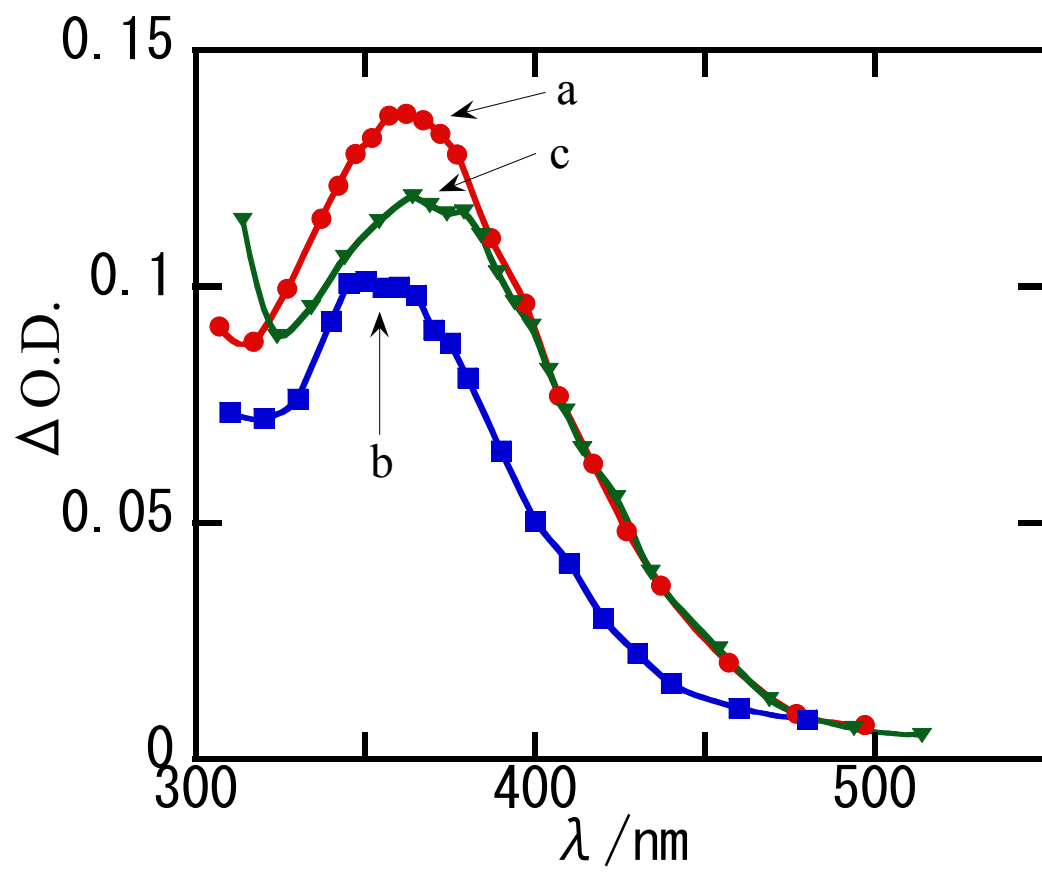


Figure 1

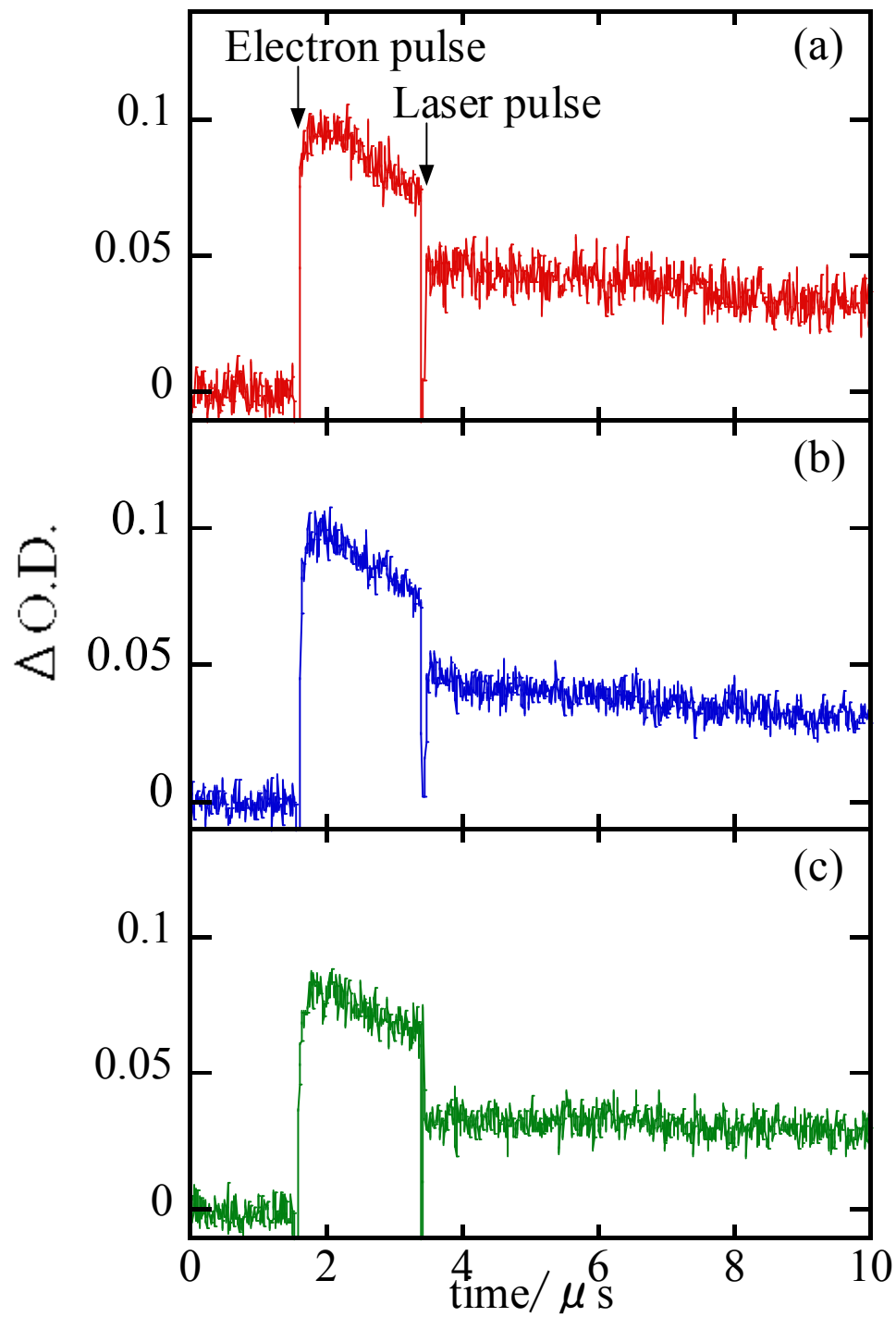


Figure 2

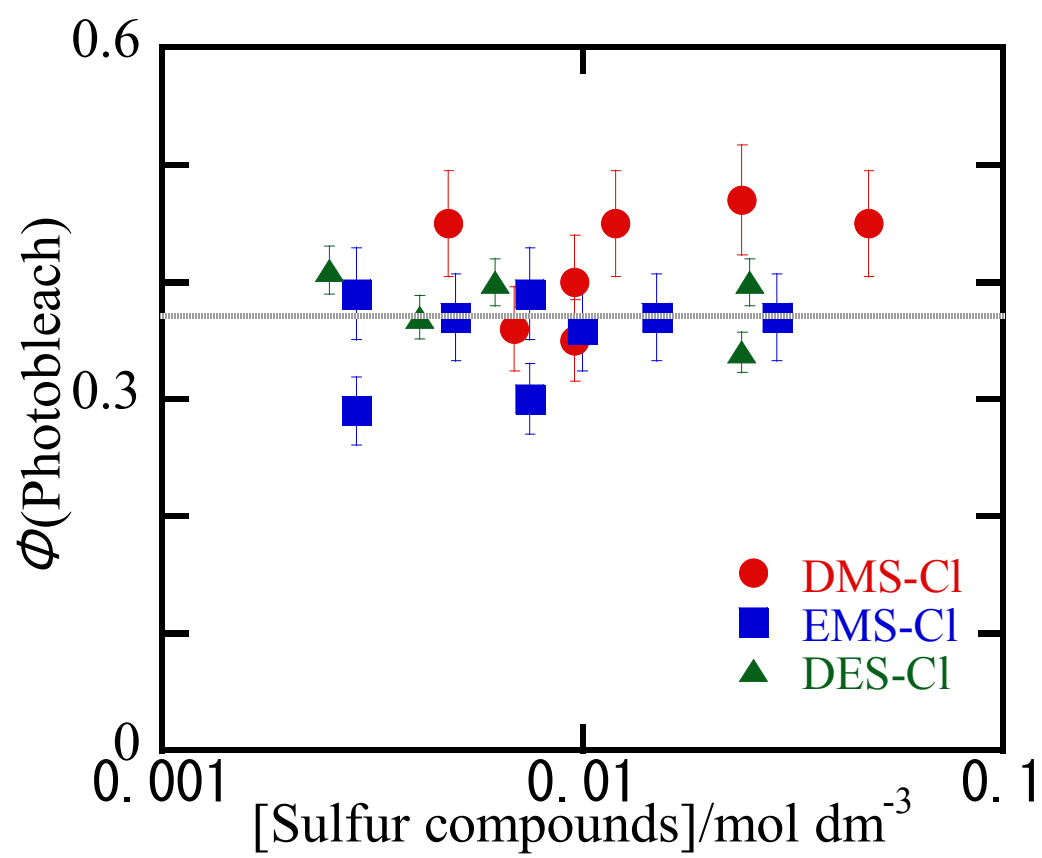


Figure 3

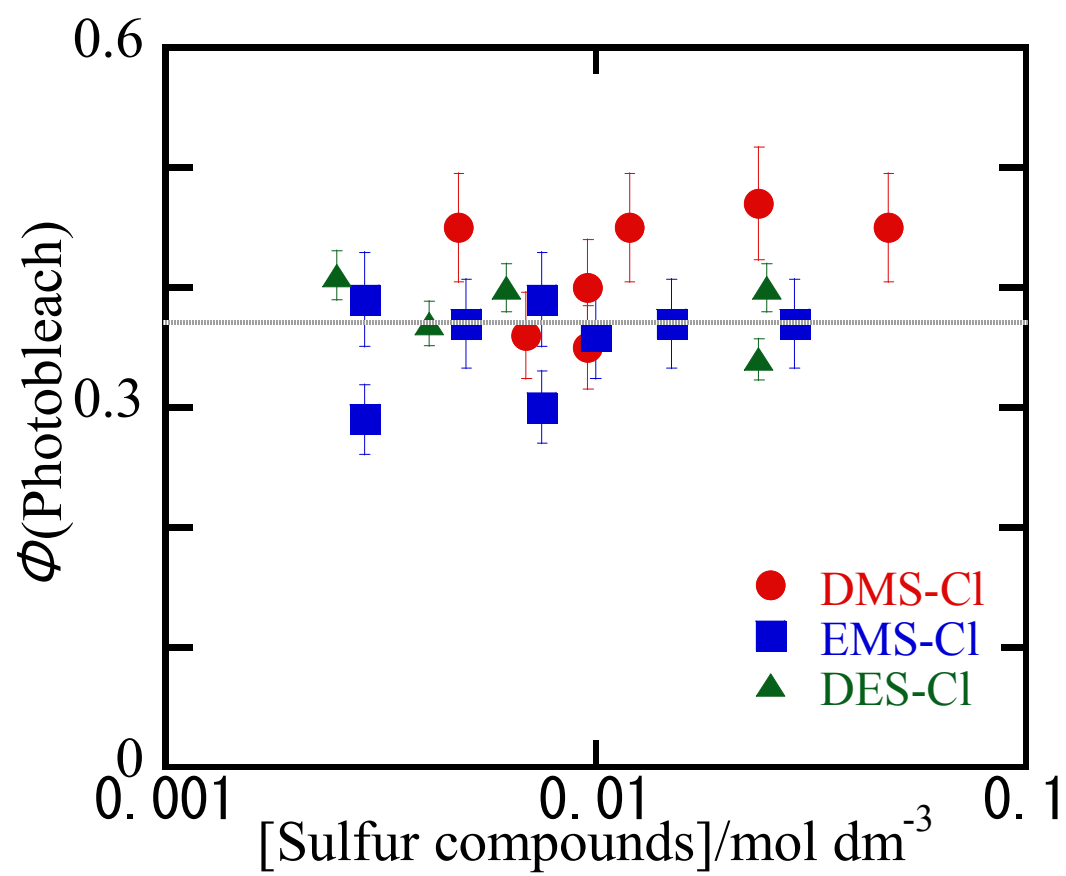


Figure 4