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Photochemistry of CS₂/Cl Complexes
-Combined Pulse Radiolysis-Laser Flash Photolysis Studies-

[Photochemistry of CS₂/Cl complexes]

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Abstract

Complexes of chlorine atoms with carbon disulfide (CS_2) were produced by pulse radiolysis of CS_2 in halocarbons and photochemical reactions were studied by laser flash photolysis. Excitation of CS_2/Cl complexes was resulted in rapid and permanent photobleaching. The photobleaching of CS_2/Cl complexes is due to intermolecular chlorine atom abstraction in CCl_4 with a quantum yield of 0.04, while it is ascribed to hydrogen atom abstraction in 1,2-dichloroethane with a quantum yield of 0.21. The effects of additives were discussed based on the bond dissociation energy.

Keywords: CS_2/Cl complex; Pulse radiolysis; Laser flash photolysis; Intermolecular hydrogen abstraction

1. Introduction

Chlorine atom complexes with arenes or carbon disulfide (CS_2) have been shown to be transient species which have high tertiary/primary selectivity in chlorination reactions of 2,3-dimethylbutane (Russell, 1958a, 1958b). The spectroscopic and kinetic studies of these complexes have been conducted extensively (Ingold et al., 1990; Chateaufneuf, 1993). While those studies have been carried out based on mainly the analyses of products induced by photochlorination of 2,3-dimethylbutane, more direct kinetic measurements of the selectivity of the hydrogen abstraction from various alcohols by free chlorine atoms (Sumiyoshi and Katayama, 1992), benzene/ Cl π -complexes (Sumiyoshi, 1997), and CS_2/Cl complexes (Sumiyoshi et al., 2005a) have been conducted using pulse radiolysis and structure-reactivity relationship analysis. The partial reactivity analysis of the reaction

rate constants predicted reaction rate constants toward alcohols in agreement with the experimental ones within ± 5 , ± 12 , and $\pm 22\%$ for free chlorine atoms, benzene/Cl complexes, and CS₂/Cl complexes respectively. Then, estimated tertiary/primary rate constant ratios are 1.7, 4.0, and 8.2 at α -position and 1.2, 5.2, and 6.8 at β -position for free chlorine atoms, benzene/Cl complexes, and CS₂/Cl complexes respectively. Thus there have been a lot of studies concerning the reactivity and the selectivity of the chlorine atom and its complexes.

In this paper we studied photochemical reactions of CS₂/Cl complexes using a combined pulse radiolysis-laser flash photolysis technique. This experimental 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, chlorine atom π -complexes with diphenyl sulfide (DPS) and various arenes have been characterized by photochemical studies. While the excitation of mesitylene/Cl π -complexes leads to photobleaching due to intramolecular hydrogen abstraction, excited DPS/Cl π -complexes exclusively undergo intermolecular hydrogen abstraction (Sumiyoshi et al., 1992, 1993). The reaction modes were found to depend on the bond dissociation energies of related atoms. The effects of the number and positions of substituents on the photochemical reactions have been investigated for a series of methyl-, ethyl-, and methoxy-substituted benzenes. The variety of the photobleaching quantum yields was found to be dependent on the bond dissociation energies of the related atoms. The structure of π -complexes was discussed in connection with the effects of the number and positions of substituents (Wu et al., 1996, 1997).

While, photochemistry of π -complexes of the chlorine atom with substituted benzenes have been studied extensively, the photochemical study of σ -complexes of chlorine atoms is rare. Very recently, photochemical reactions of σ -complexes of chlorine atoms with

dimethyl sulfoxide (DMSO) have been examined and the intermolecular hydrogen abstraction has been observed as a exclusive photoreaction of the DMSO/Cl complexes. The solvent dependent quantum yields have been ascribed to the specific solvation effect of DMSO as described in the preliminary report (Sumiyoshi et al., 2005b). The present experimental results show that the photochemical reactions of CS₂/Cl complexes can be described by intermolecular hydrogen and chlorine abstraction reactions depending on the solvents. The effects of additives were studied in detail and the reaction mechanism is discussed based on the bond dissociation energies of the related molecules.

2. Experimental

2.1. Materials

Carbon disulfide from Nacalai Tesque and alcohols from Wako Junyaku were available as high-grade commercial product and were used without further purification. Carbon tetrachloride, 1,2-dichloroethane (spectral grade), 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 a Teflon bulb prior to irradiation. Argon of ultrahigh purity was obtained from Hoxan.

2.2. Irradiation

The CS₂/Cl complexes were produced by pulse radiolysis performed 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 have been carried out using the pulse radiolysis-laser flash photolysis system with a time resolution of 10 ns described before (Sumiyoshi et al., 1993). Due to the short optical path length (0.6 cm) of this system, the electron pulse with duration of 50 ns and the dose up to 160 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 a Nd:YAG laser (Quanta-Ray, DCR-11). The dose per pulse was measured using the KSCN dosimeter (Fielden and Holm, 1970). Actinometry was performed with deaerated benzene solutions of benzophenone ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) containing naphthalene ($1.0 \times 10^{-1} \text{ mol dm}^{-3}$). The optical absorption of the naphthalene triplets formed by energy transfer from the benzophenone triplets was measured [$\epsilon_{425 \text{ nm}} = 1.32 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (Bensasson and Land, 1971), $\Phi = 1.0$ (Lamola and Hammond, 1965)]. The maximum laser output per pulse was 10 mJ. The transient signals were recorded with an Iwatsu DM901 digitizer and transferred to an NEC PC98 computer for storage and analysis. All experiments were carried out at room temperature ($16 \pm 2 \text{ }^\circ\text{C}$). The experimental uncertainty is $\pm 10\%$ for the quantum yields of photobleaching.

3. Results and Discussion

3.1. Formation of CS_2/Cl Complexes

Fig. 1 shows transient absorption spectrum observed 0.5 μs after pulse radiolysis of $1.25 \times 10^{-2} \text{ mol dm}^{-3} \text{ CS}_2$ in argon saturated CCl_4 , exhibiting absorption maxima at 370 and 490 nm which are identical with that of CS_2/Cl complexes reported previously (Chateaufneuf,

1993). Both bands decay in a similar manner. Applying the radiation chemical yield of the chlorine atom in CCl_4 to be $0.17 \mu\text{mol J}^{-1}$ as reported before (Sumiyoshi et al., 1993), the extinction coefficient of CS_2/Cl complexes in their ground state was estimated to be $8100 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ at the absorption maximum (370 nm). The extinction coefficients at other wavelengths were calculated based on the observed transient spectra of the CS_2/Cl complexes.

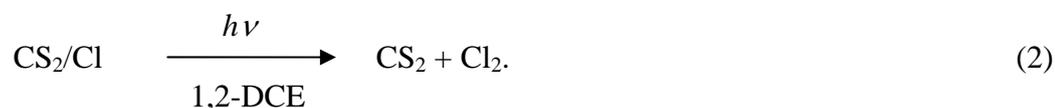
The spectral property of the CS_2/Cl complexes is quite similar with that of the benzene/ Cl π -complex ($\lambda_{\text{max}} = 320$ and 490 nm) (Chateauneuf, 1993) and those of substituted benzene/ Cl complexes (Raner et al., 1989), however, it is quite different from those of σ -complexes such as DMSO/Cl ($\lambda_{\text{max}} = 400$ nm) (Sumiyoshi and Katayama, 1990) and pyridine/ Cl complexes ($\lambda_{\text{max}} = 334$ nm) (Breslow et al., 1987). Recently detailed study on the structure of CS_2/Cl has been carried out using transient resonance Raman spectroscopy and density functional theory calculations indicating that the $\text{S}=\text{C}=\text{S}\cdots\text{Cl}$ complex which has dual π - and σ -bonding character is responsible for the 370 nm transient absorption band (Wang et al., 2002). This bonding character was found to be able to explain not only the intermediate tertiary/primary selectivity between the π -bonded benzene/ Cl complex and the σ -bonded pyridine/ Cl complex, but also the close similarity between the benzene/ Cl ($\lambda_{\text{max}} = 320$ and 490 nm) and CS_2/Cl ($\lambda_{\text{max}} = 370$ and 490 nm) transient absorption spectra.

3.2. Photochemistry of CS_2/Cl complexes

Fig. 2 shows kinetic traces obtained by pulse radiolysis (PR), flash photolysis (FP), and combined pulse radiolysis-flash photolysis (PR+FP) of deaerated $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ CS_2 in CCl_4 and in 1,2-dichloroethane (1,2-DCE). Since the kinetic traces were monitored at 370 nm, the scattered laser light (355 nm) gave the spike signals as can be seen in Fig. 2

(FP and PR+FP). Due to the low time resolution of the detection system (10 ns) and the spike signals, it was not possible to observe dissociation and reformation of the CS₂/Cl complexes. The flash photolysis of CS₂/Cl complexes results in a rapid and permanent photobleaching in both solvents, however, the quantum yields are quite different, i.e. 0.04 in CCl₄ and 0.21 in 1,2-DCE. Since, the same quantum yields can be expected independent on the solvent for the intramolecular photoreactions as observed in the case of excited mesitylene/Cl complexes (Sumiyoshi et al., 1992, 1993), this relatively large difference in the quantum yields strongly indicates that the excited CS₂/Cl complexes undergo mainly intermolecular reactions with the solvent but not unimolecular reactions. Similar solvent dependence has been observed for diphenyl sulfide/Cl complexes (Sumiyoshi et al., 1992, 1993). The quantum yields of intermolecular hydrogen abstraction by excited diphenyl sulfide/Cl complexes are reported to be 0 in CCl₄ and 0.05 in 1,2-DCE. On the contrary, quantum yields obtained for intermolecular chlorine atom abstraction by excited 9-xanthenyl radicals are 0.29 in CCl₄ and 0.04 in 1,2-DCE (Sumiyoshi et al., 1997, 2000).

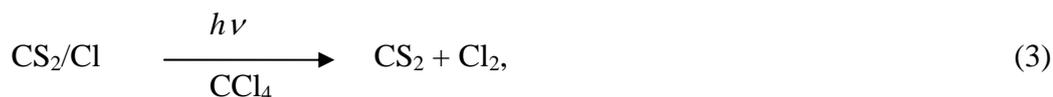
In 1,2-DCE, the following two intermolecular reactions (1) and (2) can be expected for the excited CS₂/Cl complexes:



Bond dissociation energies of chlorinated ethanes have been calculated by *ab initio* molecular orbital methods (Seetula, 1998). The obtained values for 1,2-DCE are 407.3 and 338.9 kJ mol⁻¹ for the C-H bond and C-Cl bond respectively. Considering the bond dissociation energy of H-Cl (431 kJ mol⁻¹) and Cl-Cl (242.58) (Lide, 1995), reaction (1) is exothermic (-23.7) but reaction (2) is endothermic (96.32). Consequently, it is concluded

that intermolecular hydrogen abstraction (reaction (1)) is the main photochemical process in 1,2-DCE.

The photobleaching observed in CCl₄ solutions could be attributed to the following reactions (3) or (4):



Both reactions are endothermic, 63.32 for reaction (3) and 153.5 kJ mol⁻¹ for reaction (4), based on the known bond dissociation energies: 305.9 (Cl-CCl₃), 242.58 (Cl-Cl), 430.5 (S-CS), and 277.0 kJ mol⁻¹ (Cl-S) (Lide, 1995). Although the excitation laser photon energy (3.49 eV) is large enough to afford the necessary energy of 0.656 and 1.59 eV for reactions (3) and (4) respectively, reaction (4) is much less probable. Therefore, it is strongly suggested that the photobleaching is induced by the intermolecular chlorine atom abstraction (reaction (3)) in CCl₄. The intermolecular chlorine atom abstraction has been evidenced previously for excited 9-xanthenyl and 9-thioxanthenyl radicals (Sumiyoshi et al., 1997, 2000, 2001), excited diphenylmethyl radicals (Scaiano et al., 1985), and excited 9-phenylxanthenyl radicals (Minto and Das, 1989).

The intermolecular hydrogen abstraction was further substantiated based on the experimental results obtained by adding various hydrogen containing molecules to CCl₄ solutions. Fig. 3 shows the effects of cyclohexane on photobleaching quantum yields in CCl₄. With increasing concentration of cyclohexane from 1.3 × 10⁻² to 5.1 × 10⁻² mol dm⁻³, the quantum yield increased from 0.06 to 0.29 as shown in Fig. 4. These results strongly support the exclusive intermolecular hydrogen abstraction (reaction (5)) from cyclohexane:



The lower bond dissociation energy of cyclohexyl-H ($399.6 \text{ kJ mol}^{-1}$) (Lide, 1995) than that of 1,2-DCE (407.3) may result in the higher quantum yields ($\Phi > 0.21$) in the concentration range of $[\text{cyclohexane}] > 4 \times 10^{-2} \text{ mol dm}^{-3}$. Similar results were obtained with various alcohols. The effects of alcohols are illustrated in Fig. 5. On addition of $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ methanol, ethanol, 1-propanol, and 1-pentanol to CCl_4 solutions of $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ CS_2 , increased quantum yields of photobleaching were obtained to be 0.07, 0.11, 0.14, and 0.17 respectively. The intermolecular hydrogen abstraction from the primary-, secondary-, and tertiary-position of alcohols are exothermic (-42.62 – -21.62) (Lide, 1995). The observed increase of quantum yields may due to the statistical effects. The quantum yields increased almost linearly with increasing the number of alkyl-H atoms of alcohols as shown in Fig. 6. These results again support the exclusive intermolecular hydrogen abstraction (reaction (6)) from alcohols:



The reactivities of ground state benzene/Cl π -complexes toward alcohols (Sumiyoshi, 1997) are about one order higher than those of ground state CS_2/Cl complexes (Sumiyoshi et al., 2005a). On the contrary, in the excited state the benzene/Cl π -complexes are much less reactive than CS_2/Cl complexes. The excited benzene/Cl π -complexes do not undergo intramolecular or intermolecular reactions (Wu et al., 1997). Methyl substituted benzenes undergo intramolecular hydrogen abstraction exclusively. The quantum yields increases with increasing substituents from 0.05 for toluene to 0.15 for hexamethylbenzene. However, these quantum yields are much lower than those of intermolecular hydrogen

abstraction of CS₂/Cl complexes ($\Phi=0.21$ in 1,2-DCE), indicating the stable nature of aromatic compounds toward photolysis and radiolysis (Spinks and Woods, 1990).

4. Conclusion

Present results demonstrate that excited CS₂/Cl complexes undergo intermolecular chlorine atom abstraction in CCl₄ with $\Phi = 0.04$, while they undergo intermolecular hydrogen abstraction exclusively in 1,2-DCE with $\Phi=0.21$. The reactivity of excited CS₂/Cl complexes are much higher than those of excited benzene/Cl and substituted benzenes/Cl π -complexes on the contrary to the reactivities of their ground state.

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Figure Captions

Figure 1. Transient absorption spectra observed in pulse radiolysis experiments. Spectrum of CS₂/Cl complexes recorded 0.5 μs after pulse radiolysis of 1.25 x 10⁻² mol dm⁻³ CS₂ in CCl₄ saturated with argon at an absorbed dose of 130 Gy/pulse.

Figure 2. Kinetic traces observed at 370 nm by pulse radiolysis-laser flash photolysis ($\lambda_{\text{inc}} = 355 \text{ nm}$) of 2.5 x 10⁻² mol dm⁻³ CS₂ (a) in CCl₄, and (b) in 1,2-DCE. Absorbed dose was 150 Gy/pulse. Laser intensity was 10 mJ/pulse.

Figure 3. Kinetic traces observed by combined pulse radiolysis-laser flash photolysis of 2.5 x 10⁻² mol dm⁻³ CS₂ in CCl₄ in the presence of cyclohexane. Cyclohexane concentration: (a) 1.3 x 10⁻², (b) 2.5 x 10⁻², (c) 3.8 x 10⁻², (d) 5.1 x 10⁻² mol dm⁻³. Absorbed dose was 156 Gy/pulse. Laser intensity was 10 mJ/pulse.

Figure 4. Dependence of the quantum yields of photobleaching of CS₂/Cl complexes in CCl₄ on cyclohexane concentrations.

Figure 5. Kinetic traces observed by combined pulse radiolysis-laser flash photolysis of 2.5 x 10⁻² mol dm⁻³ CS₂ in CCl₄ in the presence of 2.5 x 10⁻² mol dm⁻³ alcohols. Alcohol: (a) methanol, (b) ethanol, (c) 1-propanol, (d) 1-pentanol. Absorbed dose was 150 Gy/pulse. Laser intensity was 10 mJ/pulse.

Figure 6. Dependence of the quantum yields of photobleaching of CS₂/Cl complexes on the number of alkyl-H-atoms in alcohols.

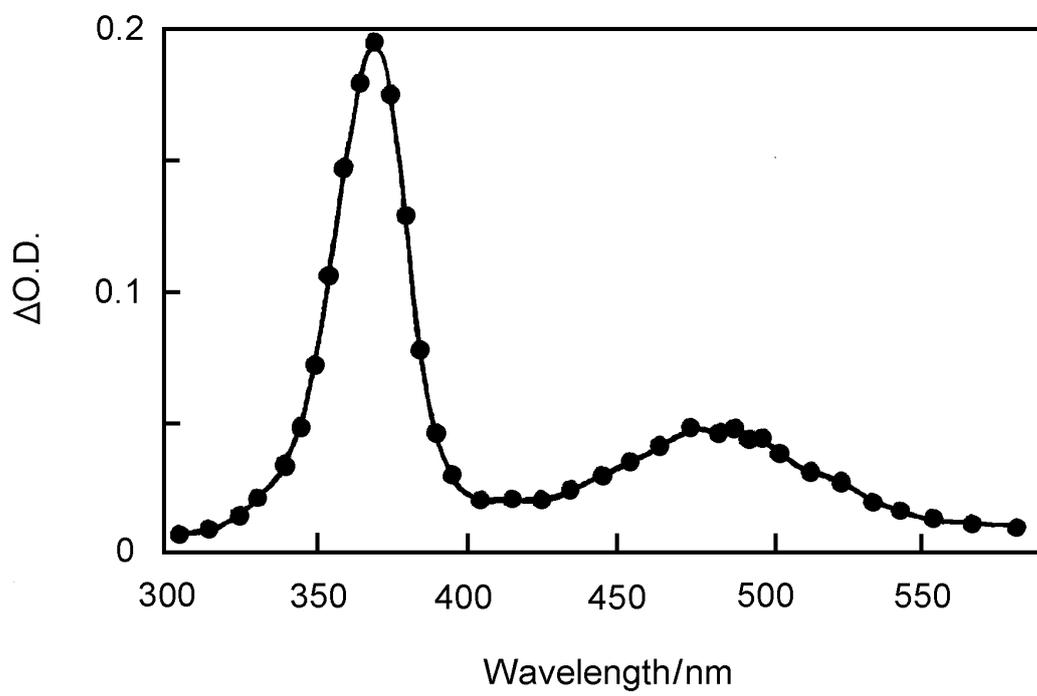


Figure 1 Sumiyoshi et al.

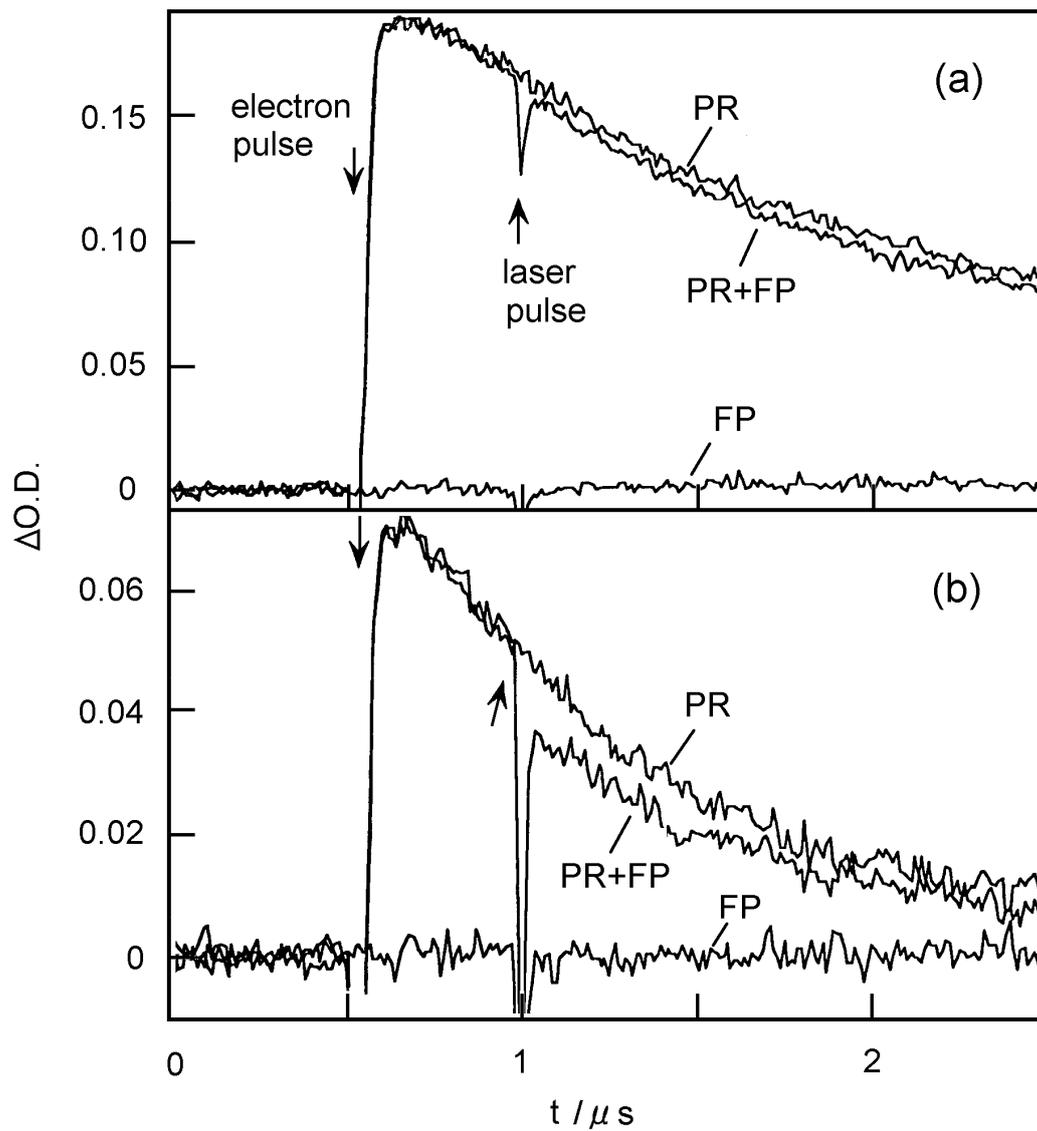


Figure 2 Sumiyoshi et al.

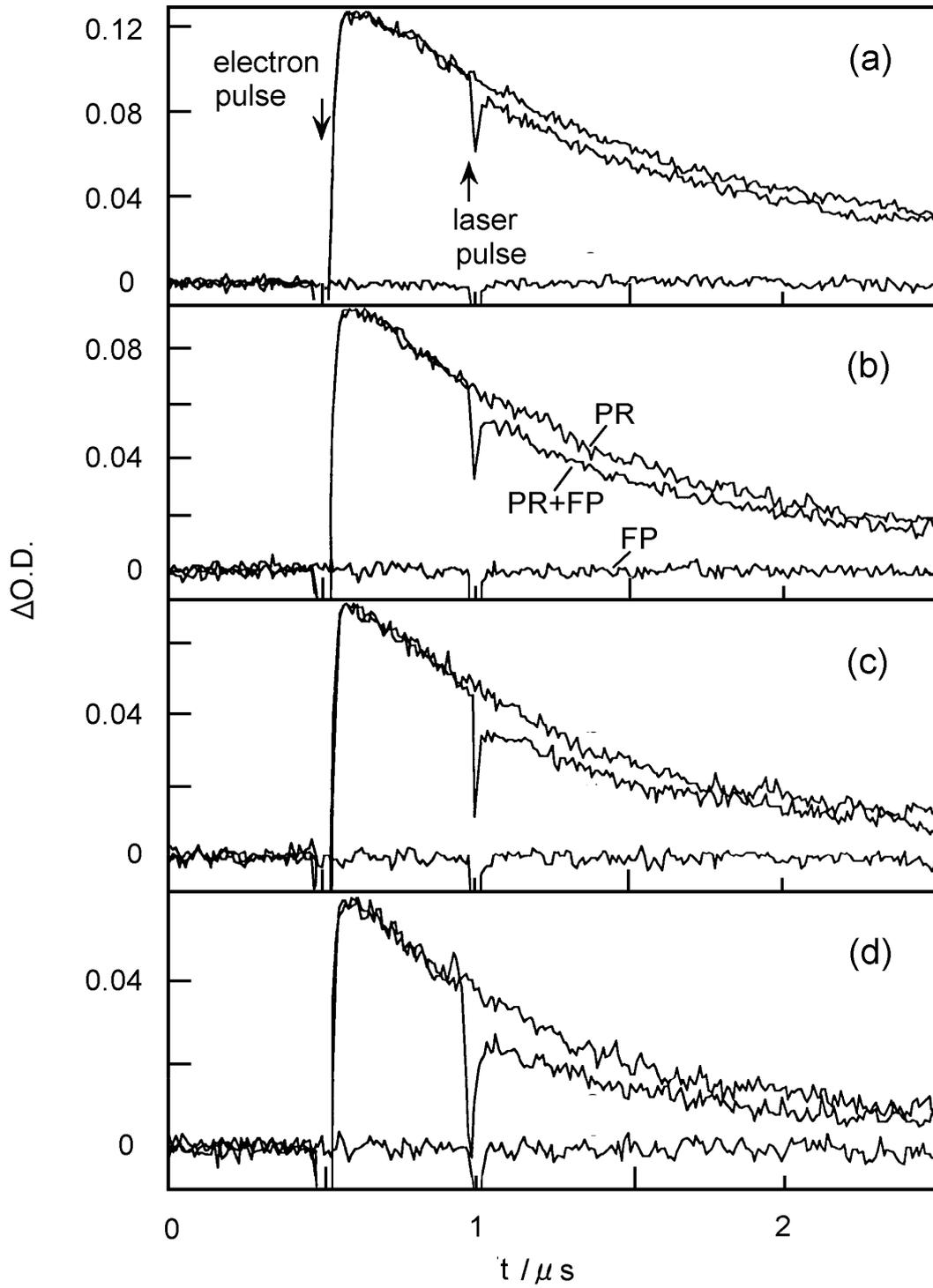


Figure 3 Sumiyoshi et al.

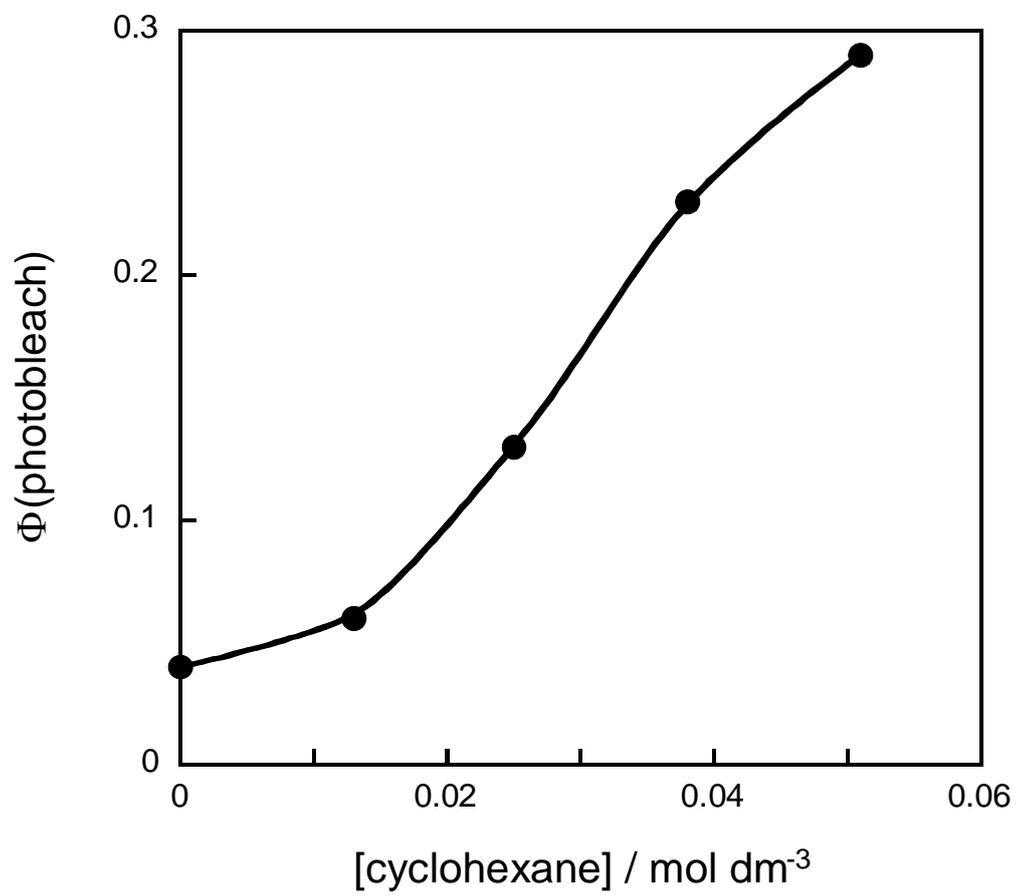


Figure 4 Sumiyoshi et al.

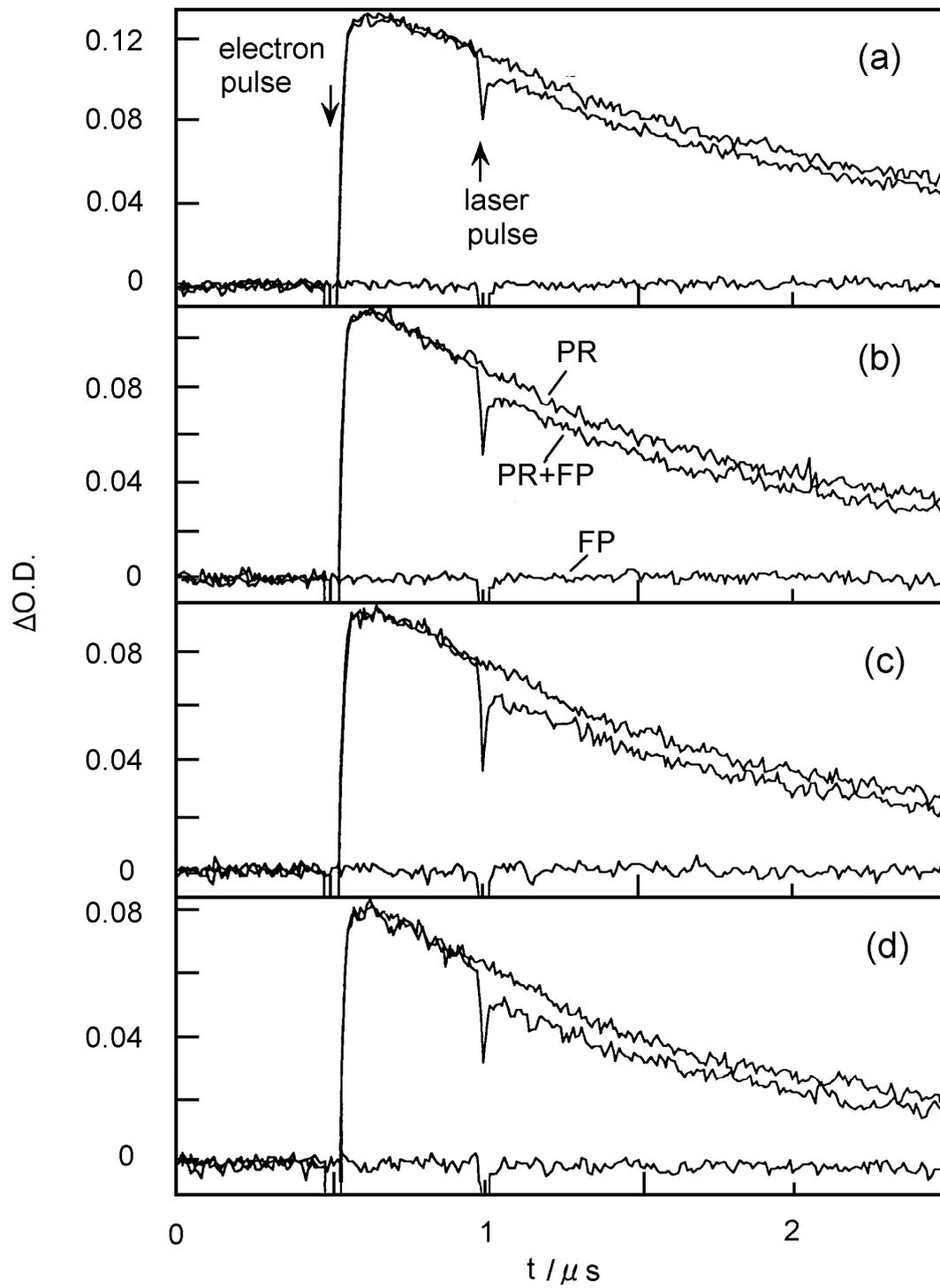


Figure 5 Sumiyoshi et al

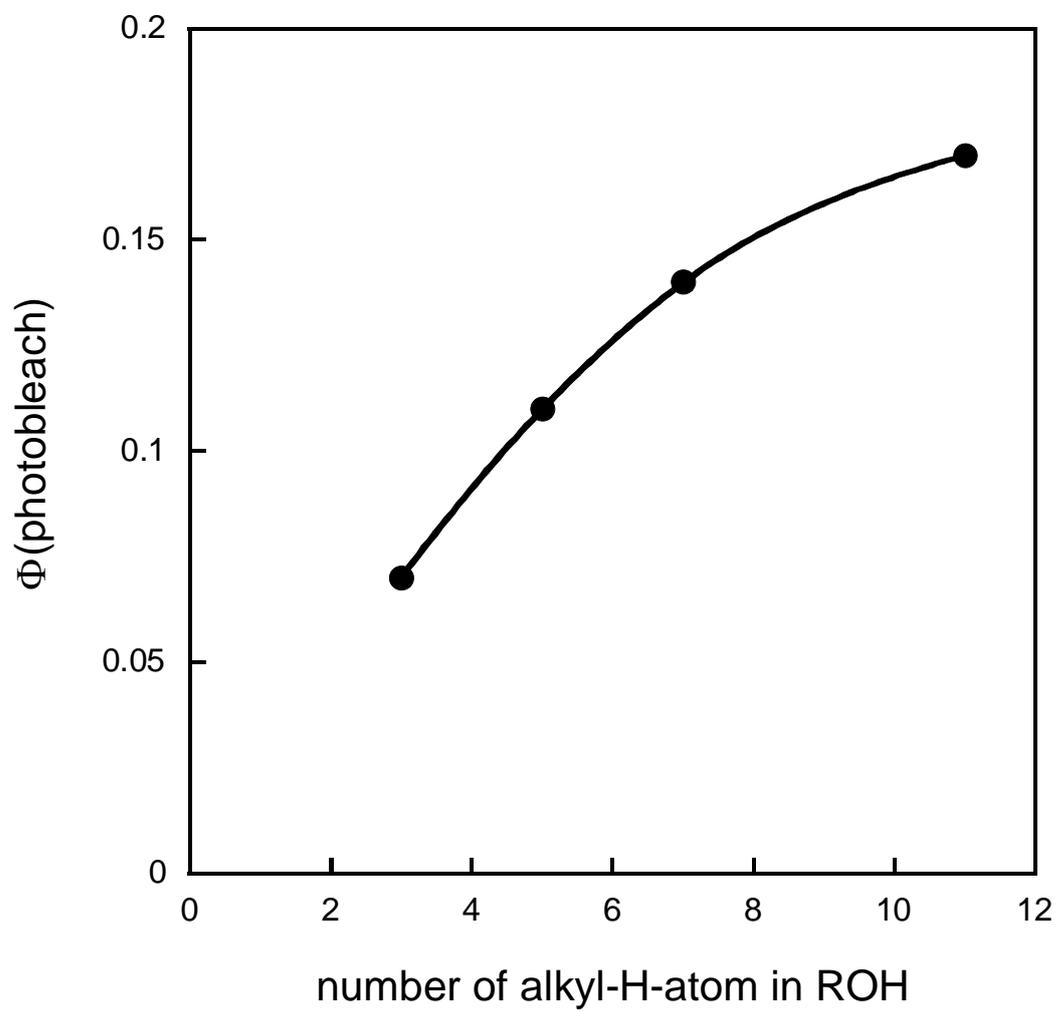


Figure 6 Sumiyoshi et al.