Reaction of CS_2/Cl complexes with alcohols studied by pulse radiolysis

[Reaction of CS_2/Cl complex]

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Abstract

The reactivity and selectivity of carbon disulfide-chlorine atom complex (CS_2/Cl) for hydrogen atom abstraction from various alcohols were studied by pulse radiolysis technique in carbon tetrachloride at room temperature. The measured absolute rate constants were in the range from 4.0×10^6 for methanol to 3.5×10^7 dm^3 mol^{-1} s^{-1} for cyclopentanol. The hydrogen abstraction selectivity was calculated based on the analysis of partial reactivities. The tertiary/primary selectivities were determined to be 8.2 for α-position and 6.8 for β-position of alcohols.
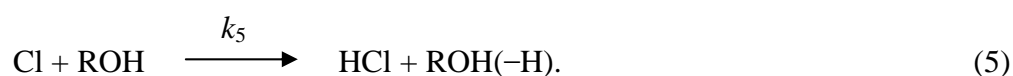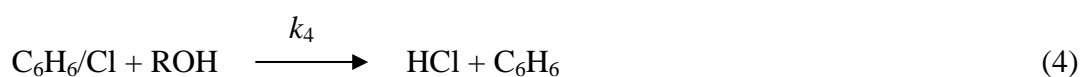
1. Introduction

The increased selectivity of tertiary to primary hydrogen abstraction in the photochlorination of 2,3-dimethylbutane in the presence of arenes or carbon disulfide (CS_2) has been explained in terms of low reactive and high selective complex formation such as arene/Cl and CS_2/Cl (Russell, 1958a, 1958b). The spectroscopic and kinetic studies of the CS_2/Cl complex showed the transient absorption spectra with a maximum around 370 nm with a shoulder at 490 nm, and the spectral similarity between the CS_2/Cl and benzene/Cl and the intermediate equilibrium constants for the CS_2/Cl formation reaction comparing the π-bonded benzene/Cl and σ-bonded pyridine/Cl complexes were discussed in connection with the structural nature of the complexes (Chateauneuf, 1993). While detailed studies of the tertiary/primary selectivity for hydrogen abstraction have been carried out for chlorine atom complexes of benzene (Bunce et al., 1985) and substituted benzenes based on the product analysis (Raner et al., 1989), the selectivity studies were limited to 2, 3-dimethybutane.

Direct kinetic measurements of the selectivity of hydrogen abstraction from various

alcohols for free chlorine atoms and benzene/Cl complexes (Sumiyoshi and Katayama, 1992; Sumiyoshi, 1997) have been carried out. The rate constants for the reaction of free chlorine atoms with 25 alcohols were determined applying a competition kinetic method taking the absorption of the dimethyl sulfoxide/chlorine atom complex (Sumiyoshi and Katayama, 1987, 1990a, 1990b; Alfassi et al., 1989; Kishore and Asmus, 1991) as a reference system, with a bimolecular rate constant of 7.0×10^{9} dm^3 mol^{-1} s^{-1} for the reaction of the free chlorine atom with dimethyl sulfoxide (Sumiyoshi and Katayama, 1987). The reaction rate constants thus obtained were assumed to be the sum of the partial reaction rate constants as had been applied for the reaction of hydroxyl radicals with aliphatic compounds including a series of alcohols in water (Anbar et al., 1966). The partial reaction rate constants of each C−H bond in the alcohol molecules were estimated and the sum of them gave the reaction rate constants agree well with the experimental values (Sumiyoshi and Katayama, 1992).

The reaction rate constants of benzene/chlorine atom complexes with alcohols were obtained by the kinetic measurements and computer simulations with the reaction set of (1) − (5) (Sumiyoshi, 1997).

$$Cl + C_6H_6 \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad C_6H_6/Cl \tag{1}$$

$$Cl \quad \xrightarrow{k_2} \quad product \tag{2}$$

$$C_6H_6/Cl \quad \xrightarrow{k_3} \quad product \tag{3}$$

$$C_6H_6/Cl + ROH \quad \xrightarrow{k_4} \quad HCl + C_6H_6 \tag{4}$$

$$Cl + ROH \quad \xrightarrow{k_5} \quad HCl + ROH(-H). \tag{5}$$

The partial reaction rate constants were calculated based on the estimated k_4 values. The experimental results showed the higher tertiary/primary selectivities of benzene/Cl complexes than those of free chlorine atoms (4.0 for the benzene/Cl complex, 1.7 for free chlorine atoms at α-position).

In the course of our studies involving hydrogen abstraction reaction, we became interested in the determination of the reaction rate constants of CS_2/Cl with alcohols to obtain the selectivity data directly. In the present work, the rate constants of the reaction of CS_2/Cl with 17 alcohols were measured by kinetic method in order to compare the reactivity and selectivity with those of free chlorine atoms and benzene/Cl complexes.

2. Experimental

2.1. Materials

Carbon disulfide from Nacalai Tesque, and carbon tetrachloride and alcohols from Wako Junyaku were available as high-grade commercial product and were used without further purification. Argon of ultrahigh purity was obtained from Hoxan. Dilute solutions in rectangular quartz cells were deaerated by bubbling argon and sealed with a bulb prior to irradiation.
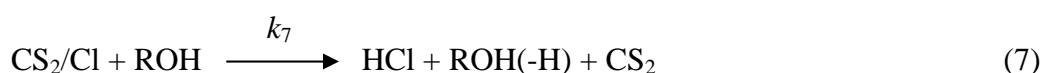
2.2. Irradiation

The pulse radiolysis experiments were performed using 10 ns, 45 MeV electron pulses from a S-band linear accelerator (Mitsubishi) at Hokkaido University delivering the dose up to 100 Gy per pulse. The optical path length of the irradiation cell was 1 cm. The dose per pulse was measured using the KSCN dosimeter (Fielden and Holm, 1970). The transient optical 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 ℃).

3. Results and Discussion

3.1. Pulse radiolysis of CS_2 in carbon tetrachloride

Pulse radiolysis of deaerated CCl_4 solutions containing CS_2 leads dominantly to the CS_2/Cl complexes. Figure 1 shows the transient absorption spectra observed immediately and at 50 μs after pulse radiolysis of 1.25×10^{-2} mol dm^{-3} CS_2 in argon saturated CCl_4. The UV-Vis spectrum recorded immediately after pulse exhibiting absorption maxima at 370 and ~485 nm is identical with that of CS_2/Cl complexes reported previously (Chateauneuf, 1993). After the decay of the CS_2/Cl complex, absorption spectrum with a peak below 350 nm remained (Fig. 1b). The insert shows kinetic traces recorded at 370 (Fig. 1c) and 490 nm (Fig. 1d). Both bands decay in a similar manner, but as can be seen in Fig. 1c the kinetic trace at 370 nm is the superposition of the long-lived transient absorption.

The decay traces of CS_2/Cl complexes cannot be described by single first-order kinetics or second-order kinetics. However, upon addition of alcohols the decay was accelerated and followed first-order kinetics. Typical time profiles of the optical absorption at 370 nm obtained on addition of 2-pentanol are shown in Fig. 2. Considering the reaction rate constant of the CS_2/Cl complex formation (reaction (6)), $k_6 = 1.7 \times 10^{10}$ M^{-1} s^{-1}, and the equilibrium constant, $K = 1900$ M^{-1}, previously reported (Chateauneuf, 1993), the formation of the CS_2/Cl complex was completed in 20 ns and the pseudo-first-order condition for reaction (7) was employed in this work; $[CS_2/Cl] \gg [ROH]$.

$$Cl + CS_2 \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} CS_2/Cl \tag{6}$$

$$CS_2/Cl + ROH \xrightarrow{k_7} HCl + ROH(-H) + CS_2 \tag{7}$$

The observed pseudo-first-order rate constants, k_{obsd}, are then described by the following

equation:

$$k_{obsd} = k_0 + k_7 \text{[ROH]} \tag{8}$$

where k_0 is the assumed first order decay rate constant of the CS_2/Cl complex in the absence of alcohols. Plots of data obtained from the decay curves by kinetic analysis according to above equation are shown in Fig. 3 for 2-pentanol (a) and cyclopentanol (b). From the slope of the straight lines the rate constants of the reaction (7) were obtained for 17 alcohols and are compiled in Table 1.

As shown in Fig. 2, the maximum optical absorption of the CS_2/Cl complex recorded immediately after the pulse decreased significantly with increasing the concentration of alcohols. Since the rate constants of the reaction of alcohols with chlorine atoms are two orders larger than those of the reaction with the CS_2/Cl complex (Table 1), the reduction of the initial yield of the CS_2/Cl complex is due to the competition reaction between alcohols and CS_2 toward chlorine atoms (reactions (5) and (6)). Provided that the product of reaction (5) does not absorb at 370 nm, then the competition can be represented by Eq. 9:

$$OD_0/OD = 1 + (k_5\text{[ROH]}/k_6\text{[CS}_2\text{]}) \tag{9}$$

where OD_0 and OD denote the maximum optical density of the 370 nm band in the absence and presence of alcohols. The rate constants for the reaction of free chlorine atoms with various alcohols, k_5, were determined previously (Sumiyoshi and Katayama, 1992) and listed in Table 1. Figure 4 shows the ratio OD_0/OD as a function of alcohol concentration in the cases of 1-, 2-, and 3-pentanol. Good linear plots were obtained for 17 alcohols under investigation. Second order reaction rate constants, k_6, thus determined are summarized in Table 1. For all alcohols listed in Table 1, almost the same values were obtained within the experimental error, $k_6 = (4.2 +\_ 0.7) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. However, these values are significantly smaller than the value $1.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ reported earlier (Chateauneuf, 1993). It should be noted that the latter value was measured by following the decay of the charge-transfer band of Cl atoms in CCl_4 with an absorption maximum at

330 nm and the growth of the 370 nm band attributed to the CS_2/Cl complex. The reactivities of transient UV-band with a peak at 330nm produced in irradiated CCl_4 toward various alcohols were measured and the rate constants have been compared with those of the free chlorine atom obtained using the competitive scavenging method (Sumiyoshi and Katayama, 1992). The values of reaction rate constants of the UV-band are nearly twice those of the free chlorine atom. In the case of the free chlorine atom, reactivities depended on the structure of alcohols, however, such effects were not observed for the UV-band. These results strongly suggest the different reactivity between the free chlorine atom and the charge-transfer complex of Cl atoms with CCl_4.

3.2. Partial reactivities of C-H bonds of alcohols toward CS_2/Cl complexes

The reactivity of the CS_2/Cl complex towards simple aliphatic alcohols in CCl_4 can be correlated with structural parameters as was done for the free chlorine atom (Sumiyoshi and Katayama, 1992) and the benzene/Cl complex (Sumiyoshi, 1997). Figure 5 shows a plot of the rate constants (k_7) for the reaction of the CS_2/Cl complex with straight chain alcohols as a function of the chain length. The linear increase of the rate constant indicates that the CS_2/Cl complex attack to every secondary C-H bond of straight chain alcohols without selectivity. However, it is interesting to note that the reactivity of alcohols depends on the structure of them rather than the molecular size. Among isomers more branched alcohols such as 2-propanol, 2-methyl-2-propanol, 2-methyl-2-butanol and 2,2-dimethyl-1-propanol have lower reactivity. On the contrary, 2-butanol, 3-methyl-2-butanol and cyclopentanol exhibit higher reactivity than the corresponding normal alcohols. These results strongly indicate the low reactivity of the primary C−H bonds and high reactivity of the secondary and tertiary C−H bonds of alcohols toward the CS_2/Cl complex. Since the CS_2/Cl complex is much less reactive than the free chlorine atom, the CS_2/Cl complex must be more selective. Therefore, we can ignore the reaction of the CS_2/Cl complex toward the hydroxyl hydrogen based on the previous experimental

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results which showed the substitution of the hydroxyl hydrogen with deuterium gives little effect on the reaction rate constants of the free chlorine atom with alcohols (Sumiyoshi and Katayama, 1992).

The more detailed structural parameters were obtained by applying the partial reactivity concept which has been successfully used to the reaction of the hydroxyl radical in aqueous solutions (Anbar et al., 1966) and the reactions of the free chlorine atom (Sumiyoshi and Katayama, 1992) and the benzene/Cl complex (Sumiyoshi, 1997) in CCl_4. Similar approaches have been also used interpret trends in reactivity of gas phase reactions. The structure-activity relationships have been derived for the abstraction of hydrogen atoms in the simple alkanes by atomic chlorine, which can then be used to predict room temperature rate constants to within 11 % (Aschmann and Atkinson, 1995).   A similar structure-activity approach has been applied to a series of halogenated alkanes and oxygenated hydrocarbons, which would allow prediction of rate constants to within a factor of 2, and on average, within 50 % of experimentally determined values (Senkan and Quam, 1992).

Partial reaction rate constants of each C−H bond as assigned to primary, secondary and tertiary bound to α-, β-, γ-, ⋯ positions in the alcohol molecules were calculated by the least squares method to obtain the best fit of the experimental rate constants.   The same rate constants for β-, γ-, δ-, ⋯ positions were assumed as in the cases of the free chlorine atom and the benzene/Cl complex (Sumiyoshi, 1997).   The partial rate constants obtained are listed in Table 2 as compared with those of the free chlorine atom and the benzene/Cl complex obtained previously.   The hydrogen abstraction rate constants of these chlorination reagents were found to vary by up to 2 orders of magnitude from the CS_2/Cl complex to the free chlorine atom.   The benzene/Cl complex has intermediate reactivity among them.   The tertiary/primary ratios at α-position are 2.7, 4.0, and 8.2 for the free chlorine atom, benzene/Cl complexes, and CS_2/Cl complexes, respectively. Similar

increase of tertiary/primary ratios (1.2, 5.2, 6.8) were observed at β-position. As expected, tertiary/primary ratios increase as the reactivity decreases. It is interesting to note the same increase of tertiary/primary ratios was reported to be ca. 1/100 and 1/50 for benzene/Cl complexes and CS_2/Cl complexes during the photochlorination of 2,3-dimethybutane (Skell et al., 1983).

The reaction rate constants calculated based on the partial reaction rate constants given in Table 2 are shown in Table 1 as k_7(calc.). The calculated reaction rate constants are in agreement with the experimental ones within +_22%, +_12%, and +_5% for CS_2/Cl complexes, benzene/Cl complexes, and the free chlorine atom, respectively. The larger uncertainty for CS_2/Cl complexes might be due to the assumption of the same partial reaction rate constants at β-, γ, δ-positions.

4.   Conclusion

Pulse radiolysis studies of CS_2 in carbon tetrachloride containing alcohols were performed to obtain direct kinetic data concerning the tertiary/primary selectivity for the hydrogen abstraction by CS_2/Cl complexes. The partial reaction rate constants were calculated based on the absolute reaction rate constants obtained with 17 alcohols. The tertiary/primary ratios are 8.2 and 6.8 for α- and β-position.

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Figure Captions

Figure 1. Transient absorption spectra observed (a) immediately and (b) 50 µs after pulse radiolysis of 1.25 x 10^{-2} mol dm^{-3} CS$_2$ in CCl$_4$ saturated with argon at an absorbed dose of 93 Gy/pulse.   The insert shows the kinetic traces monitored at (c) 370 and (d) 490 nm.

Figure 2. Decay traces of CS$_2$/Cl complexes observed at 370 nm after pulse radiolysis of 1.25 x 10^{-2} mol dm^{-3} CS$_2$ in argon-saturated CCl$_4$ containing (a) 0, (b) 4.5 x 10^{-3}, (c) 9.0 x 10^{-3}, (d) 1.3 x 10^{-2}, and (e) 1.8 x 10^{-2} mol dm^{-3} 2-pentanol.   Absorbed dose per pulse was 82 Gy.

Figure 3. Reaction of the CS$_2$/Cl complex with (a) 2-pentanol and (b) cyclopentanol. Experimental first-order reaction rate constants of the decay of the transient absorption at 370 nm vs. the alcohol concentration.

Figure 4. Plots of OD$_0$/OD vs. alcohol concentration for the competition reaction between CS$_2$ and alcohols towards chlorine atoms.   [CS$_2$] = 1.25 x 10^{-2} mol dm^{-3}; (a) 1-pentanol; (b) 2-pentanol; (c) 3-pentanol.

Figure 5. Effects of the number of carbon atoms for the reaction of alcohols with CS$_2$/Cl complexes.

Table 1.

Reaction rate constants determined by pulse radiolysis of CS_2 in CCl_4 at room temperature

Alcohol	Reaction rate constant ($M^{-1} s^{-1}$)			
	k_5 (Cl + ROH) [a]	$k_6(CS_2 + Cl)$	$k_7(CS_2/Cl + ROH)$	k_7(calc.)
methanol	2.47×10^9	4.8×10^9	4.0×10^6	4.0×10^6
ethanol	3.14×10^9	4.3×10^9	1.2×10^7	1.18×10^7
1-propanol	4.21×10^9	4.5×10^9	1.7×10^7	1.73×10^7
2-propanol	3.46×10^9	4.8×10^9	1.4×10^7	1.70×10^7
1-butanol	5.12×10^9	4.1×10^9	2.4×10^7	2.28×10^7
2-butanol	4.16×10^9	3.9×10^9	2.6×10^7	2.25×10^7
2-methyl-1-propanol	4.30×10^9	3.5×10^9	2.2×10^7	2.17×10^7
2-methyl-2-propanol	2.91×10^9	3.9×10^9	9.0×10^6	9.1×10^6
1-pentanol	5.77×10^9	4.1×10^9	2.6×10^7	2.82×10^7
2-pentanol	5.55×10^9	4.4×10^9	2.7×10^7	2.80×10^7
3-pentanol	5.06×10^9	3.9×10^9	3.1×10^7	2.80×10^7
2-methyl-1-butanol	5.37×10^9	3.9×10^9	2.3×10^7	2.72×10^7
2-methyl-2-butanol	3.94×10^9	4.5×10^9	1.4×10^7	1.46×10^7
3-methyl-1-butanol	5.59×10^9	3.7×10^9	2.8×10^7	2.72×10^7
3-methyl-2-butanol	4.59×10^9	4.1×10^9	3.4×10^7	2.69×10^7
2,2-dimethyl-1-propanol	4.56×10^9	4.0×10^9	2.1×10^7	1.79×10^7
cyclopentanol	5.29×10^9	4.2×10^9	3.5×10^7	3.29×10^7

[a] Sumiyoshi and Katayama, 1992

Table 2.

Partial reaction rate constants of CS_2/Cl complexes, benzene/Cl complexes and free chlorine atoms toward each C−H bond of alcohols in CCl_4 at room temperature

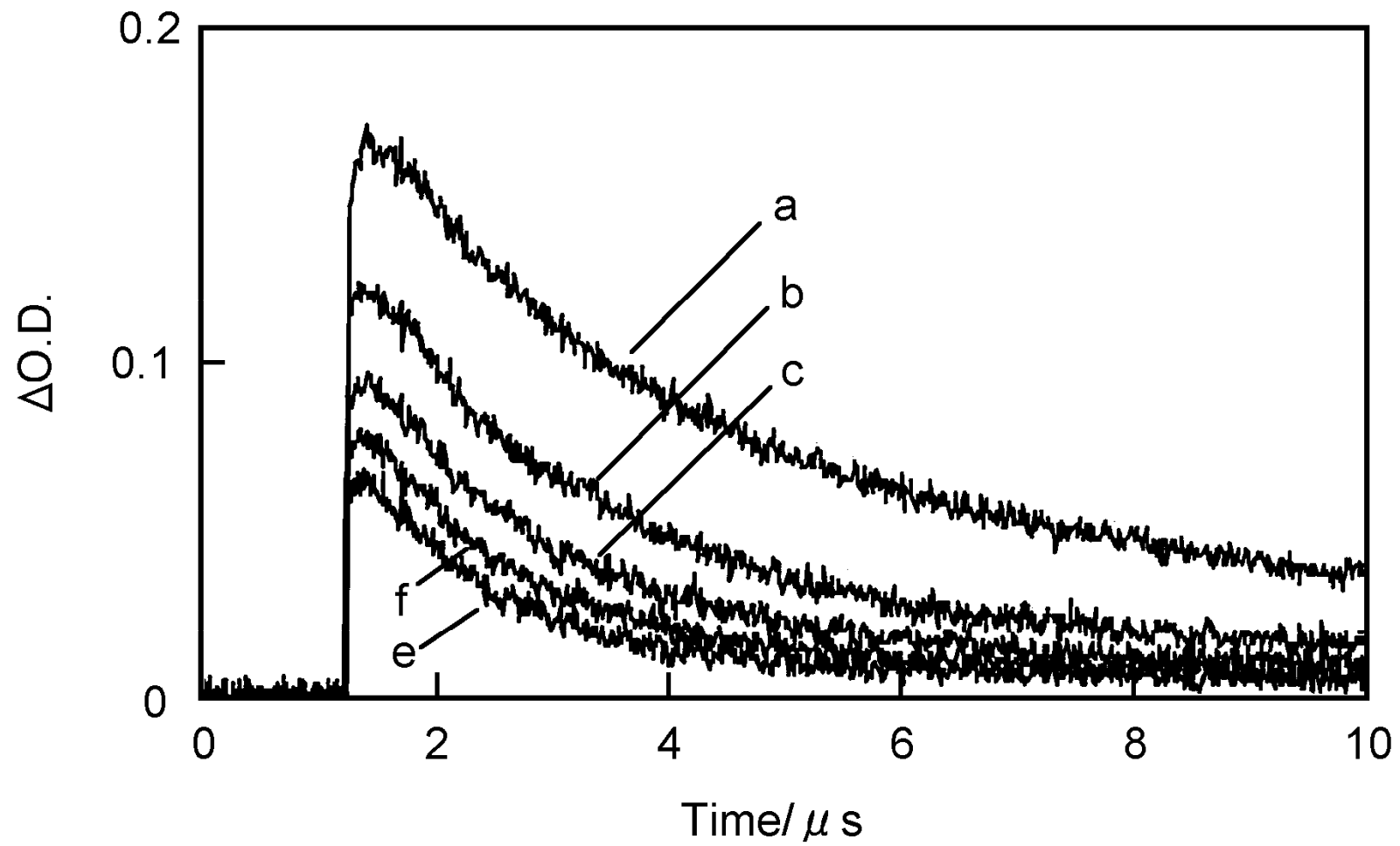| Position of C−H bond	k_p (M^{-1} s^{-1})		
	CS_2/Cl	Benzene/Cl[a]	Cl[a]
α-primary	1.33 x 10^6	2.6 x 10^7	8.23 x 16^8
α-secondary	4.39 x 10^6	5.4 x 10^7	1.04 x 16^9
α-tertiary	1.09 x 10^7	1.04 x 16^8	1.39 x 16^9
β-primary	1.01 x 16^6	9.0 x 16^6	3.19 x 16^8
β-secondary	2.74 x 10^6	2.1 x 10^7	4.93 x 16^8
β-tertiary	6.86 x 10^6	4.7 x 10^7	3.86 x 16^8

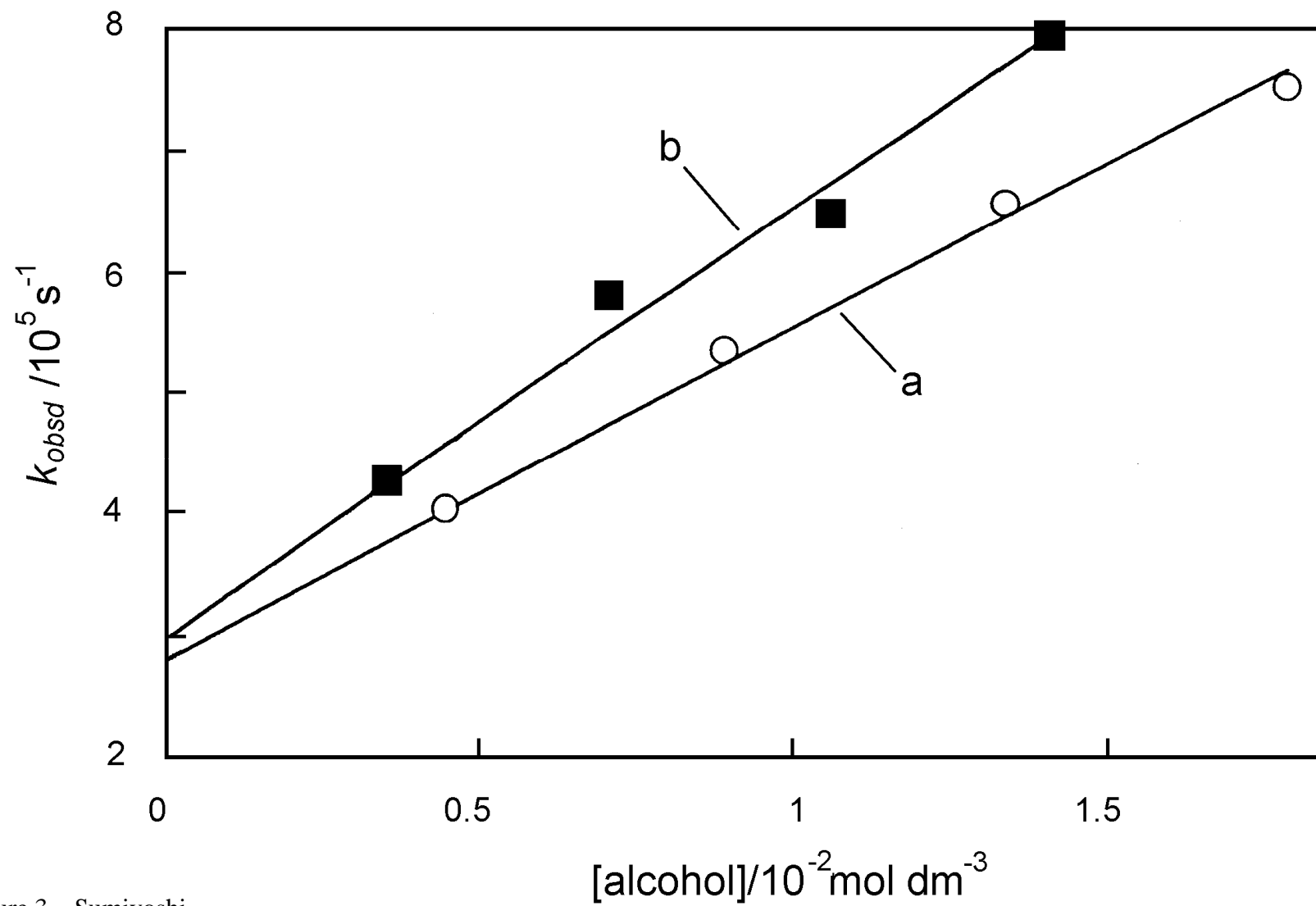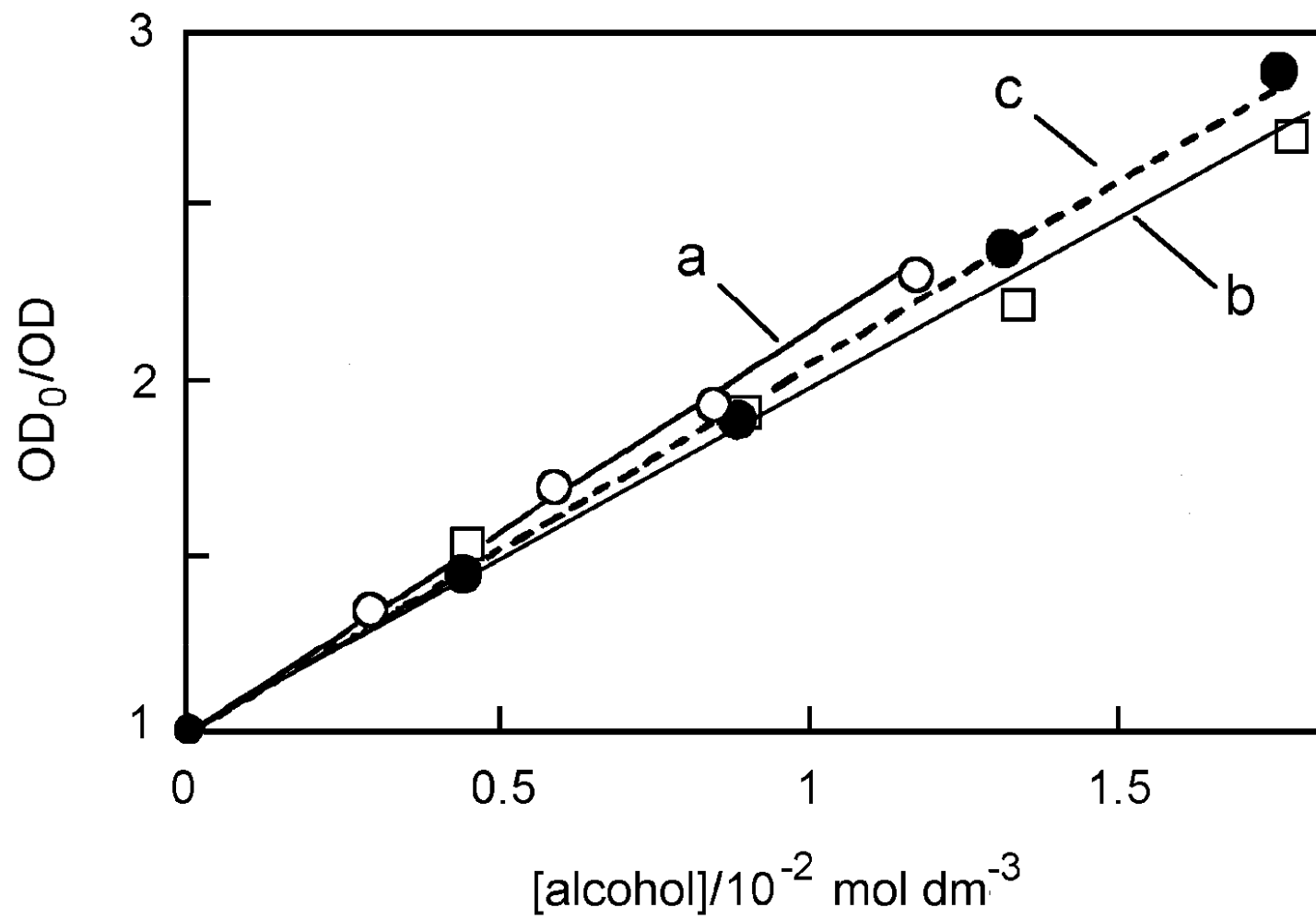[a] Sumiyoshi, 1997
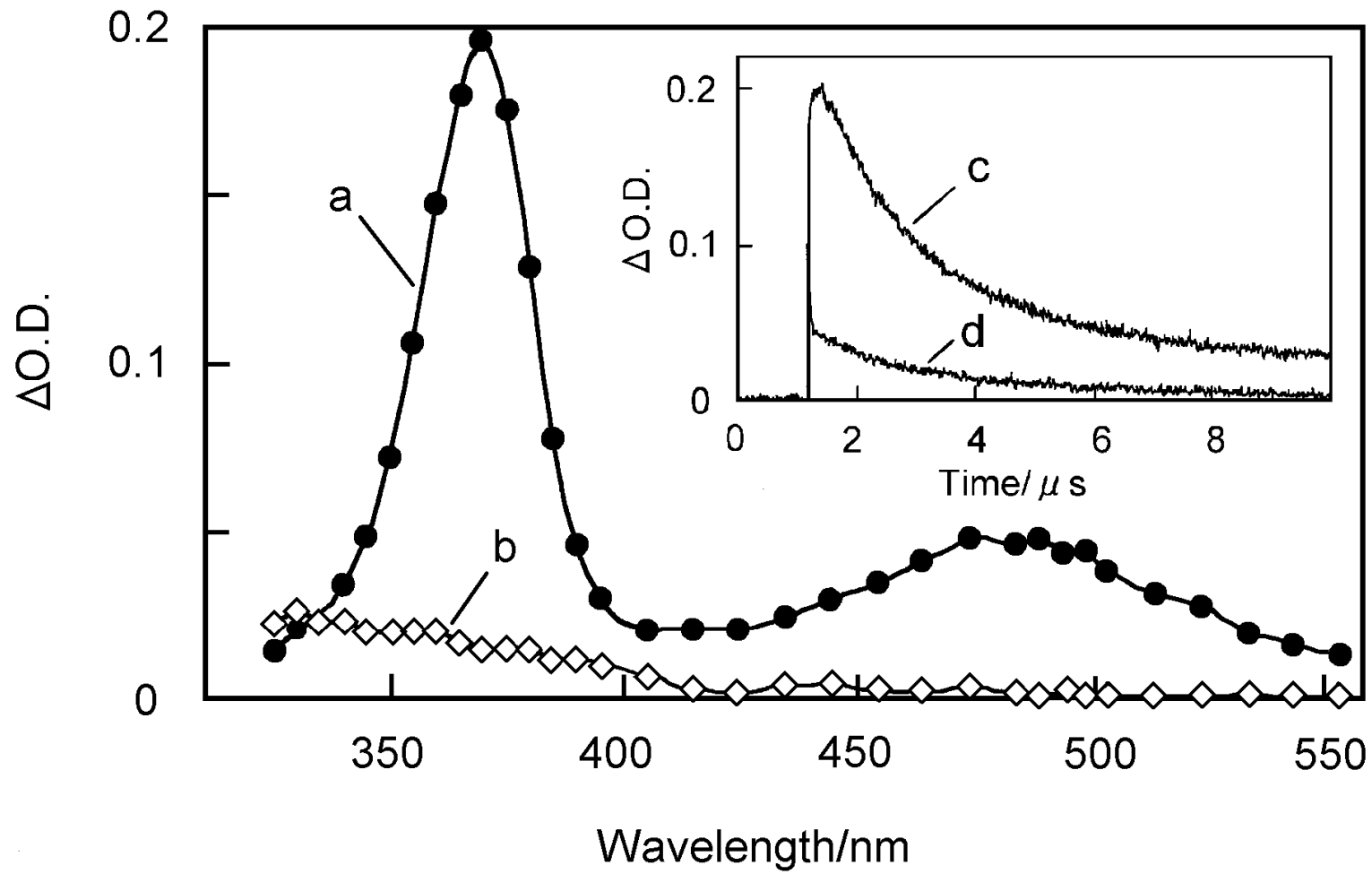
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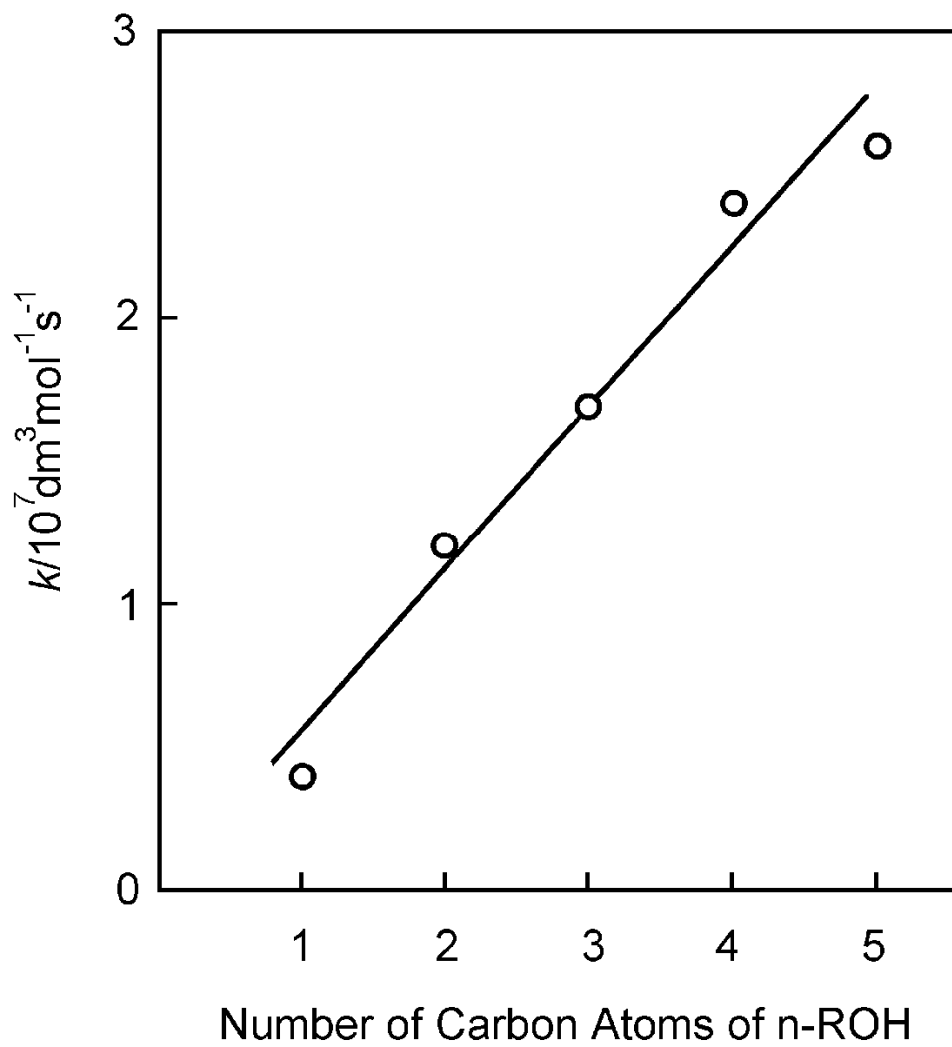
Figure 2   Sumiyoshi

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