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Pulse radiolysis studies of the reactions of bromine atoms and dimethyl sulfoxide–bromine atom complexes with alcohols

[Reaction of Br and DMSO−Br complex]

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Abstract

Dimethylsulfoxide (DMSO)−Br complexes were generated by pulse radiolysis of DMSO/bromomethane mixtures and the formation mechanism and spectral characteristics of the formed complexes were investigated in detail.   The rate constant for the reaction of bromine atoms with DMSO and the extinction coefficient of the complex were obtained to be 4.6×10^9 M^{-1} s^{-1} and 6300 M^{-1} cm^{-1} at the absorption maximum (430 nm).   Rate constants for the reaction of bromine atoms with a series of alcohols were determined in $CBrCl_3$ solutions applying a competitive kinetic method using the DMSO−Br complex as the reference system.   The obtained rate constants were $\sim$ 10^8 M^{-1} s^{-1}, one or two orders larger than those reported for highly polar solvents.   Rate constants of DMSO−Br complexes with alcohols were determined to be $\sim 10^7$ M^{-1} s^{-1}.   A comparison of the reactivities of Br atoms and DMSO−Br complexes with those of chlorine atoms and chlorine atom complexes which are ascribed to hydrogen abstracting reactants strongly indicates that hydrogen abstraction from alcohols is not the rate determining step in the case of Br atoms and DMSO−Br complexes.

Keywords: Pulse radiolysis; Rate constant; Br; DMSO−Br complex; Alcohol

1. Introduction

The formation of DMSO−Cl complexes and DMSO−Br complexes has been observed in pulse radiolysis of DMSO in both CCl_4 and $CBrCl_3$ (Sumiyoshi and Katayama, 1987). Since the absorption maxima of these complexes are in an easily detectable wavelength region, 400 nm for DMSO−Cl complexes and 430 nm for DMSO−Br complexes,

DMSO−Cl complexes have been used as a reference system to determine the rate constants for reactions of chlorine atoms with a series of alcohols in CCl_4 (Sumiyoshi et al., 1987) and with various types of organic compounds in dichloromethane (Alfassi et al., 1989). Applying structure-reactivity relationship analysis to the reaction of chlorine atoms with alcohols, the rate constants have been calculated as the sum of the partial reactivity of each C−H bond of the alcohol moiety and found to agree with the experimental results within ±5% (Sumiyoshi and Katayama, 1990a). Together with the effects of the deuterium isotope on the rate constants, the above results clearly indicate that the rate determining step is the hydrogen abstraction by the chlorine atom. The hydrogen abstraction rate constants have been compared with rate constants of the reactions for the transient UV-band peaking at 330 nm produced in CCl_4 with alcohols. The different dependence on the structure of alcohols strongly suggested that the assignment of the UV-band to chlorine atoms (Chateauneuf, 1990) is not justifiable, and instead, supports an assignment to the parent cations (Sumiyoshi and Katayama, 1992). The structure-reactivity relationship analysis has also been successfully applied to the reaction of benzene−Cl (Sumiyoshi, 1997) and CS_2−Cl complexes (Sumiyoshi et al., 2005b) with a series of alocohols, suggesting that the rate determining process is hydrogen abstraction.

While a number of studies on the reaction of bromine atoms in the gas phase have been carried out (Bierbach et al., 1999 and references cited therein), kinetic and mechanistic information available for the reaction of bromine atoms in solutions is limited (Barra and Smith, 2000 and references cited therein). Bromine atoms produced in the pulse radiolysis of neat bromoalkanes and of cyclohexane solutions of them form complexes with their parent bromo compounds since hydrogen abstraction by bromine atoms is negligibly slow (Shoute and Neta, 1990a). The bromine atom complexes were found to be capable of abstracting hydrogen atoms from only weak C−H bonds such as benzylic and allylic hydrogens in hexamethylbenzene and cyclohexene and to act as oxidants toward

p-methoxyphenol, 1,3,5-trimethoxybenzene, triphenylamine, and TMPD. The CHBr$_3$−Br complexes showed significant reactivities toward 2-propanol and 2-methy-2-propanol and the reaction mechanism was ascribed to a bromine atom transfer from the complex to the oxygen atom of the alcohols followed by the decay of the adduct via a mechanism not including hydrogen abstraction, due to the endothermic nature of the reaction (Shoute and Neta, 1990b). Rate constants for the reactions of bromine atoms with several alcohols were determined in acetonitrile by laser flash photolysis experiments and hydrogen abstraction was inferred from both the formation of HBr and the methanol/ethanol/2-propanol reactivities following the order of the C−H bond reactivities of the alcohols (Scaiano et al., 1993). The reaction of chlorine atoms can be ascribed to hydrogen abstraction from most organic molecules based on its exothermicity, while there would be no hydrogen abstraction from alcohols by bromine atoms as it is endothermic. Therefore, further detailed study on the reaction mechanism of bromine atoms with alcohols is needed

The absence of hydrogen abstraction with the bromine atom and its complexes is also supported by the results obtained by photolysis of halogen atom complexes (Sumiyoshi et al., 1993). The excited diphenyl sulfide (DPS)−Cl complexes undergo hydrogen abstraction from the solvent, i. e., intermolecular hydrogen abstraction, while DPS−Br complexes show no photochemical reactions even in the presence of cyclohexane. While intramolecular hydrogen abstraction has been shown for excited mesitylene−Cl complexes, excitation of mesitylene−Br complexes induced no photochemical reactions. These results are consistent with the hydrogen abstraction taking place only in exothermic systems.

The present work measured the rate constants of the reaction of bromine atoms and DMSO−Br complexes with a series of alcohols using the optical absorption of the DMSO−Br complex as a reference system or as a probe to understand the reaction

mechanism and to compare the reactivity and selectivity with those of free chlorine atom, CS_2–Cl σ-complexes, and benzene–Cl π-complexes.

2. Experimental

2.1. Materials

Dimethyl sulfoxide (DMSO) and carbon tetrachloride (spectrograde, Dojin) were used as received.   Carbon tetrabromide and alcohols (Wako) were provided as high-grade commercial products and were used without further purification.   KBr and KCl were guaranteed reagents.   Bromotrichloromethane ($CBrCl_3$) from Wako was purified by distillation under nitrogen flow.   Argon of ultrahigh purity was obtained from Hoxan. Dilute solutions in rectangular quartz cells were deaerated by bubbling argon and sealed with Teflon bulbs prior to irradiation.

2.2. Irradiation

The pulse radiolysis experiments were performed with 10 ns, 45 MeV electron pulses from an S-band linear accelerator (Mitsubishi) at Hokkaido University delivering doses of up to 180 Gy per pulse.   Details of the pulse radiolysis setup have been described previously (Sumiyoshi and Katayama, 1990b).   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 interfaced by GPIB for storage and analysis.   All experiments were carried out at room temperature (16 $\pm$ 2 ℃).   The
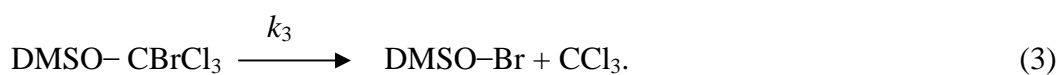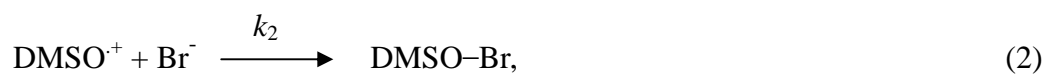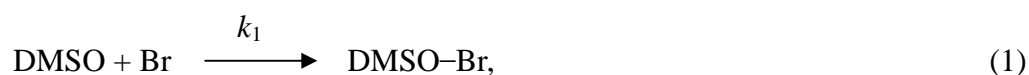
uncertainties in the determination of rate constants were within $\pm 10\%$.

3. Results and Discussion

3.1. Formation of DMSO-Br complexes

The DMSO−Br complexes were formed in the pulse radiolysis of DMSO/CBrCl$_3$ mixtures, CBr$_4$ in DMSO, and Br$^-$ in DMSO, and the kinetic and spectral properties of the DMSO−Br complexes were examined in two solvents, CBrCl$_3$ and DMSO. Irradiation of DMSO in CBrCl$_3$ and Br$^-$ in DMSO resulted in quite similar absorption spectra with a maximum at 430 nm as shown in Fig. 1. Pulse radiolysis of deaerated CBr$_4$ in DMSO also resulted in very similar spectra.

The formation processes may be described by the following three reactions by analogy with the formation mechanism of DMSO−Cl complexes in DMSO/CCl$_4$ mixtures (Sumiyoshi and Katayama, 1990b; Sumiyoshi et al., 1990):

$$\text{DMSO} + \text{Br} \xrightarrow{\quad k_1 \quad} \text{DMSO−Br}, \tag{1}$$

$$\text{DMSO}^{\cdot+} + \text{Br}^- \xrightarrow{\quad k_2 \quad} \text{DMSO−Br}, \tag{2}$$

$$\text{DMSO−CBrCl}_3 \xrightarrow{\quad k_3 \quad} \text{DMSO−Br} + \text{CCl}_3. \tag{3}$$

Reaction (1) is the main process when irradiating dilute DMSO in CBrCl$_3$. The kinetic traces obtained at different DMSO concentrations in CBrCl$_3$ are shown in Fig. 2. Grow-in traces of DMSO−Br complexes were observed superimposed on long-lived transients produced from the solvent. Kinetic analyses have been carried out with traces

of DMSO–Br complexes after subtracting the solvent originated background absorption. The observed first-order grow-in rate constants are related to k_1 and DMSO concentration by eq. (4):

$$k_{obs} = k_0 + k_1[\text{DMSO}], \tag{4}$$

where k_0 is the first-order decay rate constant of bromine atoms in the absence of DMSO (reaction (5)):

$$\text{Br} \xrightarrow{k_0} \text{product.} \tag{5}$$

From the straight line obtained according to eq. (4) as shown in Fig. 3, the rate constants of reaction (1) and (5) are obtained as $k_1=4.6\times10^9$ M^{-1} s^{-1} and $k_0=5.6\times10^6$ s^{-1}.

Reactions (2) and (3) are the main processes in the pulse radiolysis of CBr$_4$ in DMSO. The kinetic traces recorded in the pulse radiolysis of CBr$_4$ in DMSO are shown in Fig. 4. The formation of DMSO–Br complexes are observed again superimposed on a long-lived transient absorption of the solvent. The slow formation path was observed independent of CBr$_4$ concentration, since the [Br$^-$] =[DMSO$^-$] $\fallingdotseq 2\times10^{-5}$ M based on the free ion yield, 0.18 μmol J^{-1}, as reported previously (Cooper and Walker, 1971). The contribution of the fast process becomes increasingly dominant with increasing CBr$_4$ concentrations. This fast path would be induced by direct excitation of pre-associated CBr$_4$–DMSO pairs as has been suggested in the case of CCl$_4$/DMSO mixtures (Sumiyoshi et al., 1990).

Reaction (2) is the main process of formation in the irradiation of KBr in DMSO, kinetic traces of this observed at 430 nm are shown in Fig. 5. The rate constant of reaction (2) was determined under pseudo-first-order conditions in the pulse radiolysis of Br$^-$ in DMSO as $k_2=5.0\times10^9$ M^{-1} s^{-1} (Sumiyoshi and Katayama, 1990b). The DMSO–Br complexes are not stable in the presence of Br$^-$ ions ($>1\times10^3$ M) as shown in Fig. 6, and the reaction of DMSO–Br complexes with Br$^-$ leading to the formation of Br$_2^-$ with

$\lambda_{max}=360$ nm (reaction (6)) and further conversion of Br_2^- into Br_3^- with $\lambda_{max}=280$ nm (reaction (7)) have been observed previously (Sumiyoshi and Katayama, 1990b). Based on the decay traces in Fig. 6, the value of k_6 was determined under pseudo-first-order conditions to be 2.6×10^8 M^{-1} s^{-1} in DMSO:

$$DMSO{-}Br + Br^- \xrightarrow{k_6} DMSO + Br_2^-, \tag{6}$$

$$Br_2^- + Br_2^- \xrightarrow{k_7} Br_3^- + Br^-. \tag{7}$$

For dilute KBr solutions ($<1 \times 10^{-3}$ M) it may be assumed that the reaction (6) does not need to be taken into account, and the yield of DMSO$-$Br complexes in the plateau region of the grow-in traces can be related to the KBr concentration by eq. (8):

$$G_0\varepsilon/G\varepsilon = 1 + k_9/k_2[KBr], \tag{8}$$

where k_9 is the decay rate constant of DMSO$^{\cdot+}$ in the absence of added solute, G_0 is the yield of DMSO$-$Br complexes at infinite KBr concentrations, and ε is the extinction coefficient of the complexes at 430 nm:

$$DMSO^{\cdot+} \xrightarrow{k_9} product. \tag{9}$$

The double reciprocal plots yield a straight line as shown in Fig. 7. The absence of reaction (10) was reported previously (Sumiyoshi and Katayama, 1990b), and linear double reciprocal plots may also be expected for the formation of DMSO$-$Cl complexes in the radiolysis of KCl in DMSO (Fig. 7):

$$DMSO{-}Cl + Cl^- \longrightarrow DMSO + Cl_2^-. \tag{10}$$

The extinction coefficient of the DMSO$-$Cl complexes was determined as (7800 ± 50)

M^{-1} cm^{-1} at λ_{max}=400 nm in the previous study (Sumiyoshi et al., 2005a, 2006). Assuming the same G_0 values for DMSO–Cl and DMSO−Br complexes, we can determine the extinction coefficient of DMSO−Br complexes to be (6300 ± 50) M^{-1} cm^{-1} at 430 nm. The value of k_9 was estimated to be 6.5×10^5 s^{-1} from the linear plots in Fig. 7.

3.2. Reaction of Br with alcohols

The rate constants for the reactions of bromine atoms with a series of alcohols, k_{11}, were measured in CBrCl$_3$ solutions containing 1.4×10^{-3} M DMSO using a competition method applying the absorption of DMSO−Br complexes as a reference:

$$Br + ROH \xrightarrow{k_{11}} products. \tag{11}$$

The addition of alcohols caused a reduction in the initial yields of DMSO−Br complexes. Typical time profiles of the optical density at 430 nm obtained by the addition of 1-butanol are shown in Fig. 8. The optical absorption of DMSO−Br complexes in the plateau region of the kinetic traces may be related to the corresponding rate constants by eq. (12):

$$\Delta OD_0/\Delta OD = 1 + k_{11}[ROH]/(k_0 + k_1[DMSO]), \tag{12}$$

where ΔOD and ΔOD_0 are the optical densities due to DMSO−Br complexes in the presence or absence of alcohols. Fig. 9 shows plots according to eq. (12) obtained for straight chain alcohols, and the obtained k_{11} values are given in Table 1 together with the values from the literature determined in other solvents, acetonitrile (Scaiano et al., 1993; Barra and Smith, 2000), methanol (Lilie et al., 1984), and water (Lind et al., 1993; Merényl and Lind, 1994).

The reactivities of methanol, ethanol, and 2-propanol follow the order of the C−H bond dissociation energies of alcohols, 410, 389, and 381 kJ mol^{-1} (Lide, 1995), as reported elsewhere (Scaiano et al., 1993). However, the linear increase in the rate constants of normal alcohols with chain length (Sumiyoshi and Katayama, 1992; Sumiyoshi et al., 2005b), which is one sign of the hydrogen abstraction reaction from alcohols was not shown, instead, 1-propanol shows the highest reactivity. The results show that the rate constants for the reaction of bromine atoms with alcohols can not be reproduced applying structure-reactivity relationship analysis.

There were significant changes in reactivity depending on the solvent, indicating a strong solvent effect on the reactions of the bromine atom. The rate constants in CBrCl$_3$ are one and two orders higher than those in acetonitrile and water, respectively. The dielectric constants of solvents are 2.405, 33.0, 36.64, and 80.10 for CBrCl$_3$, methanol, acetonitrile, and water, respectively (Lide, 1995). This suggests that solvent polarity may play an important role in the reactivities. The negative effect of solvent on rate constants have been reported for the reactions of polar reactants and less polar transient intermediates (Ito and Matsuda, 1982, 1984). However, in the present case such effects would not play a role, since the reaction mechanism is expected to be a bromine atom addition to the oxygen atom of alcohols as proposed previously (Shoute and Neta, 1990a), the intermediate could also be polar. Log-log plots of the rate constants of Br with methanol and 2-propanol vs. dielectric constants of solvents result in straight lines as shown in Fig 10, however, an adequate explanation for this relationship is not possible here. The present results strongly indicate that hydrogen abstraction from alcohols by bromine atoms is not the rate determining step. Therefore the process of the addition of bromine atoms to alcohols may be the rate determining step:

$$Br + ROH \xrightarrow{k_{13}} ROH \cdot Br \ (ROH^+ Br^-). \tag{13}$$

3.3. Reaction of DMSO-Br complexes with alcohols

As shown in Fig. 8 the decay rate of DMSO−Br complexes became faster with increasing alcohol concentration indicating a reaction between the complexes and alcohols:

$$\text{DMSO−Br} + \text{ROH} \xrightarrow{\quad k_{14} \quad} \text{products.} \tag{14}$$

The rate constants observed under the pseudo-first-order condition, k_{obs}, are then described by the following equation:

$$k_{obs} = k_{15} + k_{14}\,[\text{ROH}] , \tag{15}$$

where k_{15} is the assumed first-order decay rate constant of the DMSO−Br complex in the absence of alcohols. Plots of the data obtained from the decay curves by kinetic analysis according to eq. (15) are shown in Fig. 10 for normal alcohols. All except 1-propanol result in very similar slopes indicating similar reactivities. The rate constants for reaction (14) were obtained for 9 alcohols and are compiled in Table 2 together with those of the CS$_2$/Cl σ-complex (Sumiyoshi et al., 2005b) and the benzene/Cl π-complex (Sumiyoshi, 1997). The reactivities of the CS$_2$/Cl complex and the benzene/Cl complex towards simple aliphatic alcohols in CCl$_4$ can be correlated with structural parameters like for the free chlorine atom (Sumiyoshi and Katayama, 1990a). The estimated rate constants are in agreement with the experimental results within ±22%, ±12%, and ±5% for CS$_2$−Cl complexes, benzene−Cl complexes, and the free chlorine atom, respectively. The present results for the DMSO−Br complex cannot be ascribed to hydrogen abstraction due to the absence of a linear increase in the rate constant with the chain length of the normal alcohols and of the structural dependence of the rate constants based on the bond dissociation energies of the C−H bonds. It must be noted that the rate constants of the

DMSO−Br complexes are smaller than those of CS$_2$−Cl complexes and benzene−Cl complexes but that the higher selectivity observed for chlorine atom complexes is missing. These results strongly indicate that hydrogen abstraction by DMSO−Br complexes is not the rate determining step, instead bromine atom transfer is the rate determining step:

$$\text{DMSO−Br + ROH} \xrightarrow{k_{16}} \text{DMSO + ROH·Br (ROH}^+\text{Br}^-). \qquad (16)$$

4. Conclusion

Pulse radiolysis studies on the kinetics and the mechanism of formation of DMSO−Br complexes in CBrCl$_3$ and DMSO were carried out. The absolute rate constants for the reaction of bromine atoms and DMSO−Br complexes with alcohols were determined in CBrCl$_3$ solutions. The rate constants were much higher than those reported for polar solvents indicating the important role of solvent polarity on the reaction of bromine atoms. The rate constants were compared with those ascribed to hydrogen abstracting reactants such as free chlorine atoms, the benzene−Cl complex, and the CS$_2$−Cl complex in CCl$_4$. As for both a linear increase in the rate constants with increasing chain length of normal alcohols and the structural dependence are absence, it is strongly indicated that the rate determining step is not hydrogen abstraction, instead a bromine atom addition process is suggested.

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Figure Captions

Fig. 1.　Transient absorption spectra of DMSO−Br complexes observed in pulse radiolysis of (○) 7.0 x 10^{-2} M DMSO in $CBrCl_3$ and (●) 1.2 x 10^{-3} M KBr in DMSO.　Solutions were saturated with argon.　Absorbed doses 168 and 142 Gy/pulse.

Fig. 2.　Kinetic traces showing DMSO−Br complex formation observed at 430 nm in the pulse radiolysis of (a) 0, (b) 3.5 x 10^{-4}, (c) 1.5 x 10^{-3}, and (d) 8.5 x 10^{-3} M DMSO in $CBrCl_3$.　Absorbed dose per pulse 160 Gy.

Fig. 3.　Pseudo-first-order rate constants for the formation DMSO−Br complexes in $CBrCl_3$ as a function of DMSO concentration.

Fig. 4.　Kinetic traces observed at 430 nm in the pulse radiolysis of (a) 0, (b) 1.5 x 10^{-3}, (c) 3.8 x 10^{-3}, (d) 7.6 x 10^{-3}, (e) 1.5 x 10^{-2}, and (f) 3.1 x 10^{-2} M CBr_4 in DMSO.　Absorbed dose per pulse 107 Gy.

Fig. 5.　Kinetic traces observed at 430 nm in the pulse radiolysis of (a) 0, (b) 5.9 x 10^{-5}, (c) 1.2 x 10^{-4}, and (d) 3.0 x 10^{-4} M KBr in DMSO.　Absorbed dose per pulse 144 Gy.

Fig. 6.　Kinetic traces observed at 430 nm in the pulse radiolysis of (a) 0, (b) 3.0 x 10^{-4}, (c) 5.9 x 10^{-4}, and (d) 1.2 x 10^{-3} mol dm^{-3} KBr in DMSO.　Absorbed dose per pulse 144 Gy.

Fig. 7.　Plot of the inverse dose normalized yields of DMSO−Br and DMSO−Cl complexes vs. the reciprocal concentration of (●) KBr at 430 nm and (□) KCl at 400 nm

in DMSO.   Absorbed doses per pulse 180 and 144 Gy.

Fig. 8.   Kinetic traces observed at 430 nm in the pulse radiolysis of 1.4×10^{-3} M DMSO in CBrCl$_3$ containing (a) 0, (b) 1.7×10^{-2}, (c) 3.4×10^{-2}, (d) 6.8×10^{-2}, and (e) 1.35×10^{-1} M 1-butanol in DMSO .   (f) Neat CBrCl$_3$.   Absorbed dose per pulse 73 Gy.

Fig. 9   Plots according to eq. (12) for the reactions of bromine atoms with ($\bigcirc$) methanol, ($\square$) ethanol, ($\bullet$) 1-propanol, ($\blacksquare$) 1-butanol, and ($\triangle$) 1-pentanol in CBrCl$_3$.

Fig. 10   Log-log plots of the reaction rate constants of bromine atoms with ($\bullet$) methanol and ($\square$) 2-propanol vs. the dielectric constants of the solvents.

Fig. 11   Observed rate constants for the reaction of DMSO$-$Br complexes with alcohols: ($\bigcirc$) methanol, ($\square$) ethanol, ($\bullet$) 1-propanol, ($\blacksquare$) 1-butanol, and ($\triangle$) 1-pentanol.

Table 1.

Rate constants (in M^{-1} s^{-1}) for the reaction of Br with alcohols determined by pulse radiolysis in solutions at room temperature

Alcohol	Solvent					
	$CBrCl_3$	Acetonitrile[a]	Acetonitrile[b]	Methanol[c]	Water[d]	Water[e]
Methanol	7.8×10^7	9.3×10^5	1.6×10^6	3×10^5		3×10^5
Ethanol	1.1×10^8	1.6×10^7				3.1×10^6
1-Propanol	2.6×10^8					
2-Propanol	1.4×10^8	4.1×10^7	3.2×10^7			6.6×10^6
1-Butanol	1.2×10^8					
2-Butanol	1.6×10^8					
2-Methyl-1-propanol	1.2×10^8	1.7×10^7				
2-Methyl-2-propanol	9.8×10^7				5×10^3	1.4×10^4
1-Pentanol	2.0×10^8	1.1×10^7				

[a]Scaiano et al., 1993.   [b]Barra and Smith, 2000.   [c]Lilie et al., 1984.   [d]Lind et al., 1993.   [e]Merényl and Lind, 1994.

Table 2.

Rate constants (in M^{-1} s^{-1}) for the reaction of DMSO−Br complexes with alcohols in $CBrCl_3$ at room temperature

Alcohol	Complex		
	DMSO−Br	CS_2−Cl[a]	Benzene−Cl[b]
Methanol	9.1×10^6	4.0×10^6	7.7×10^7
Ethanol	7.6×10^6	1.2×10^7	1.4×10^8
1-Propanol	1.7×10^7	1.7×10^7	1.7×10^8
2-Propanol	9.1×16^6	1.4×10^7	1.5×10^8
1-Butanol	8.1×10^6	2.4×10^7	2.1×10^8
2-Butanol	7.8×10^6	2.6×10^7	2.1×10^8
2-Methyl-1-propanol	8.2×10^6	2.2×10^7	2.3×10^8
2-Methyl-2-propanol	5.8×10^6	9.0×10^6	8.2×10^7
1-Pentanol	9.5×10^6	2.6×10^7	2.9×10^8

[a]Sumiyoshi et al., 2005b.　[b]Sumiyoshi, 1997.
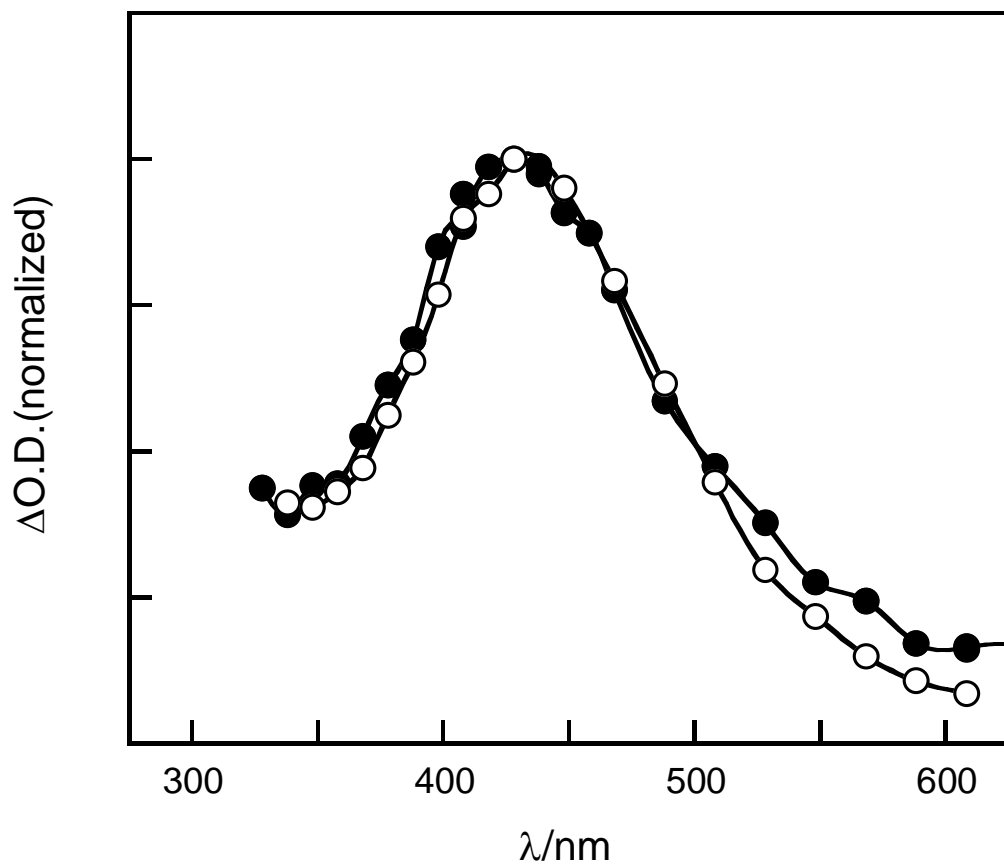
Fig. 1   Sumiyoshi et al.
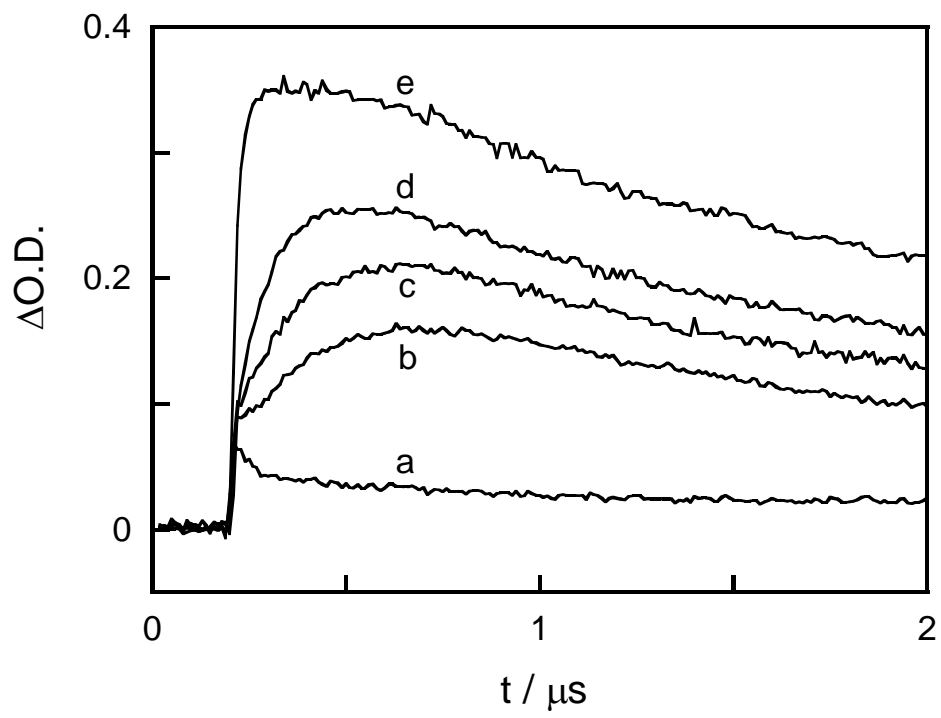
Fig. 2   Sumiyoshi et al.
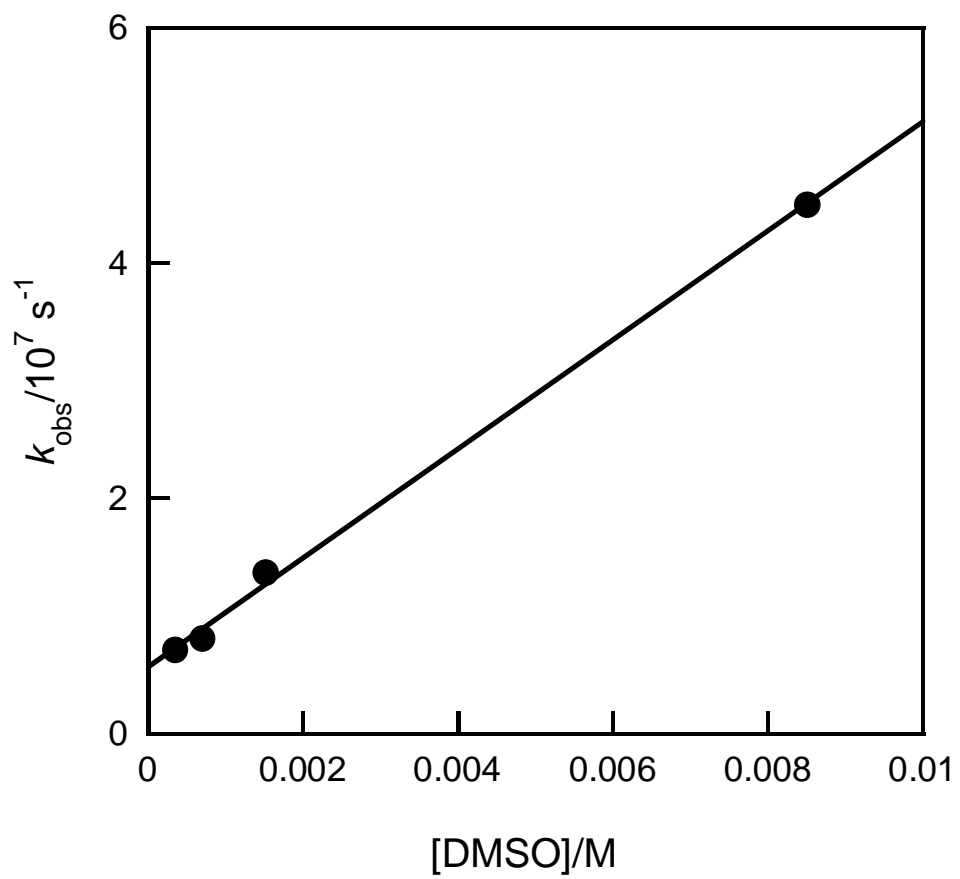
Fig. 3   Sumiyoshi et al.
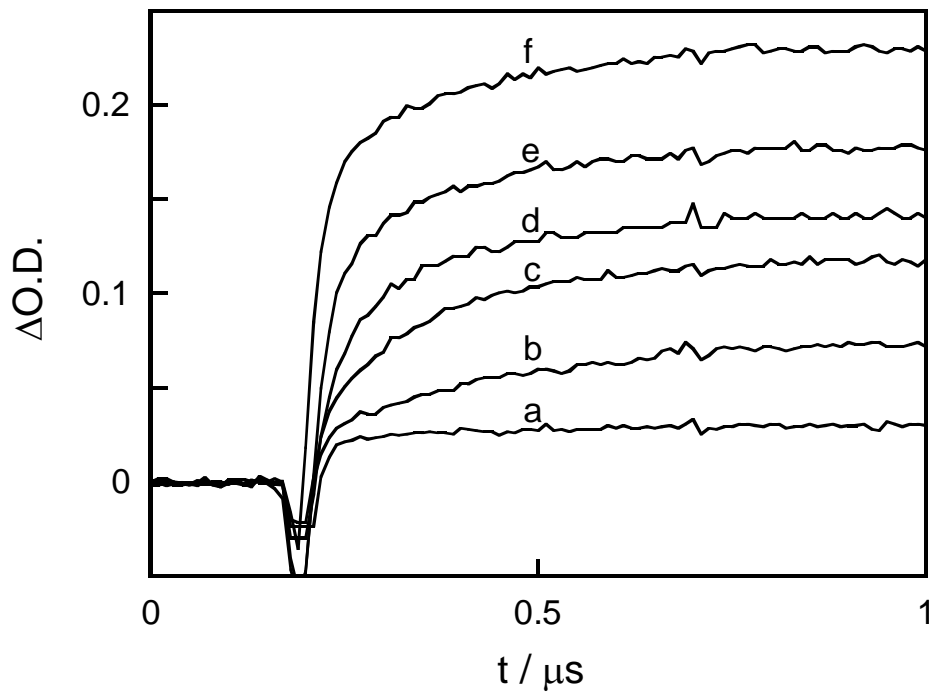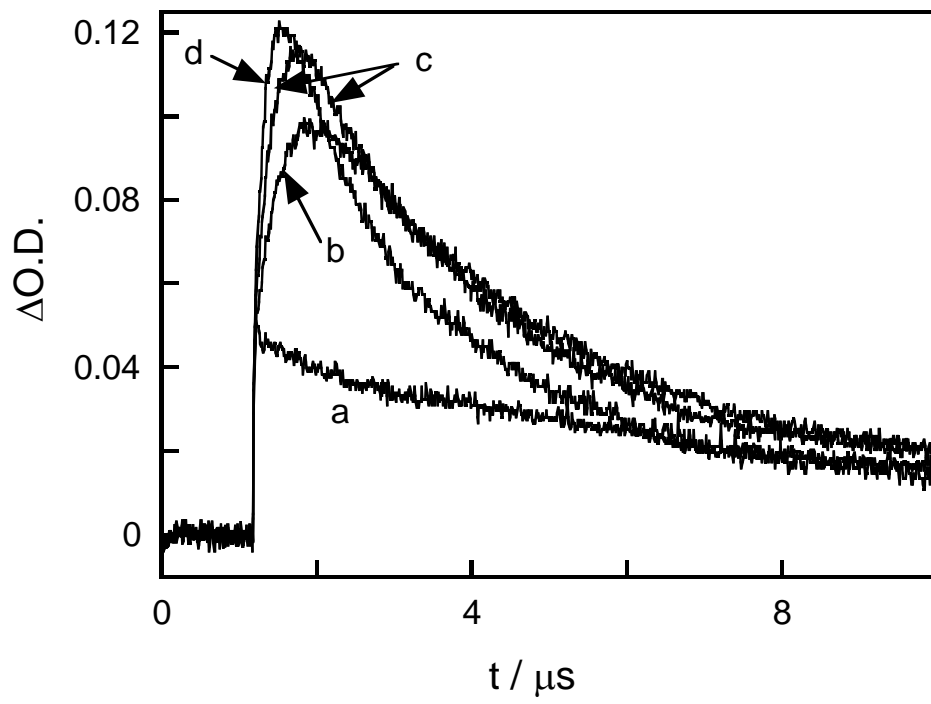
Fig. 4   Sumiyoshi et al.
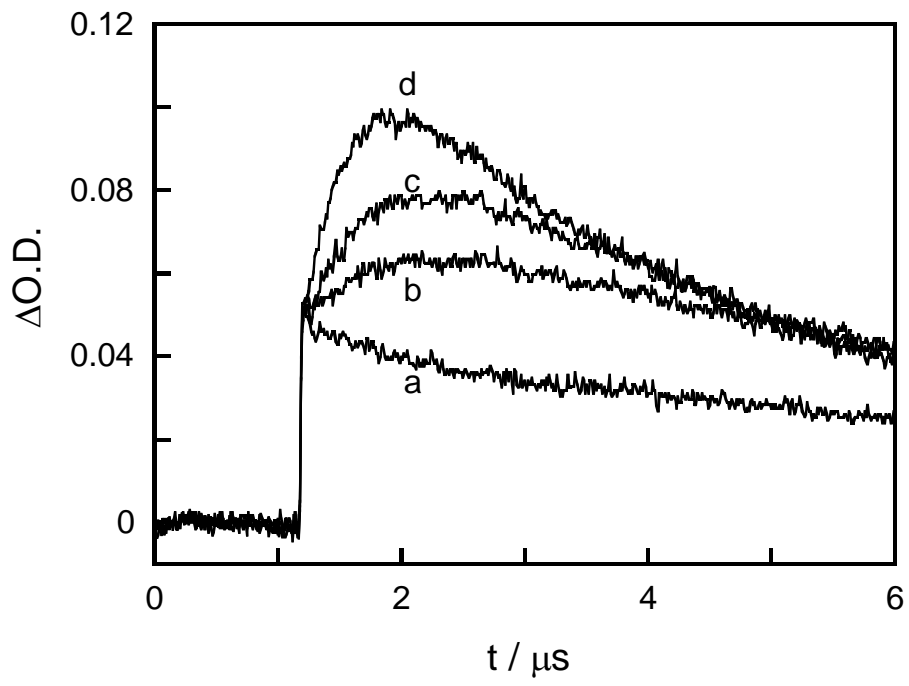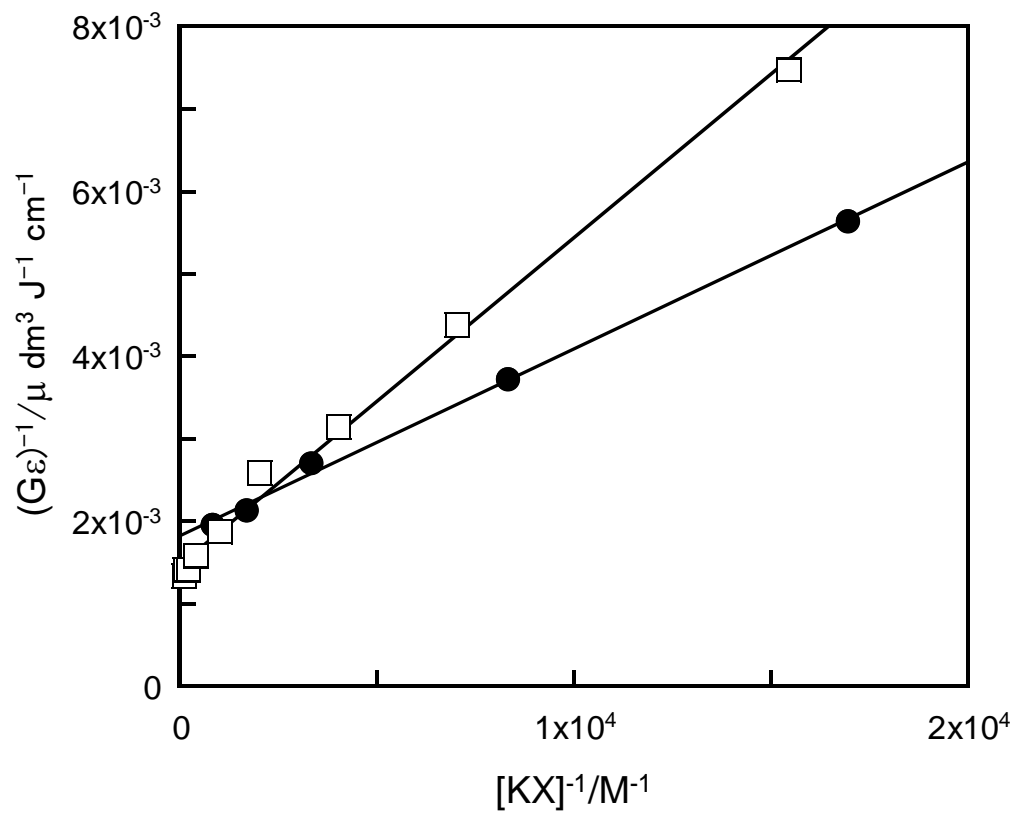
Fig. 5   Sumiyoshi et al.
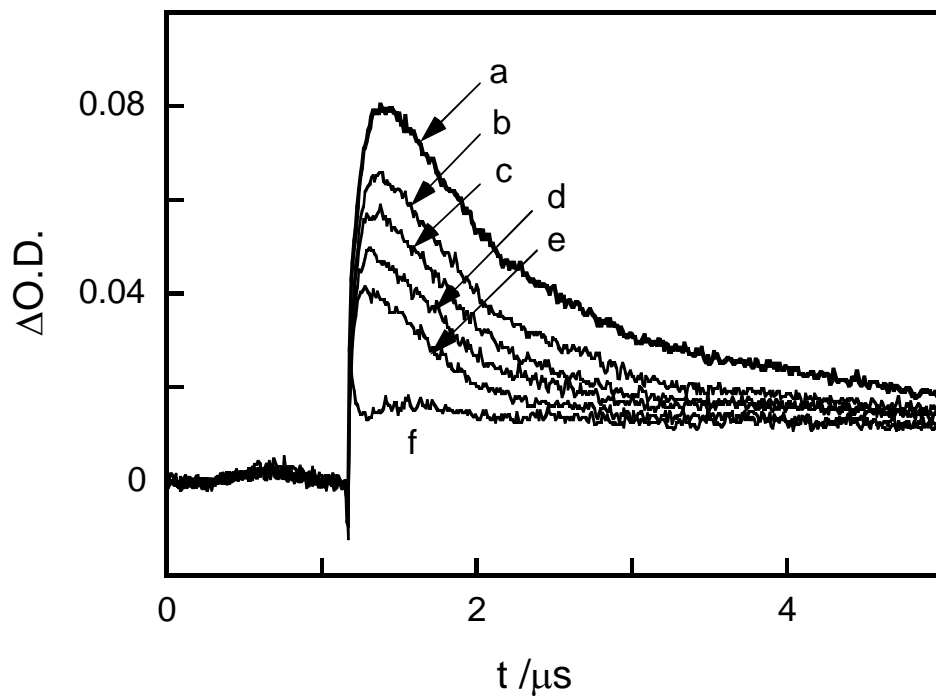
Fig. 6   Sumiyoshi et al.

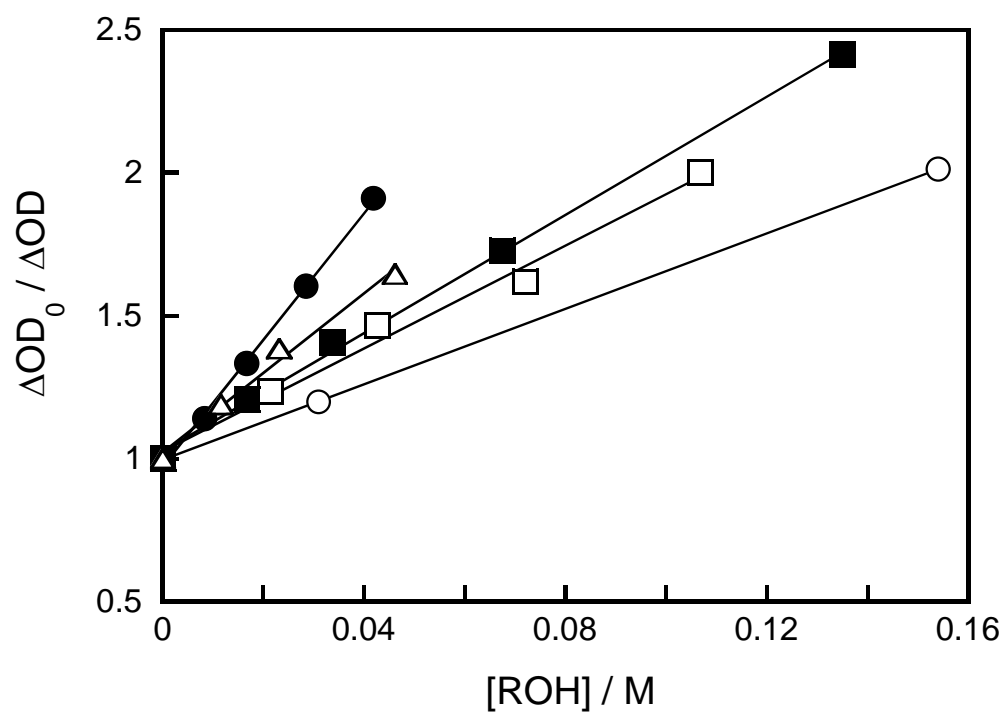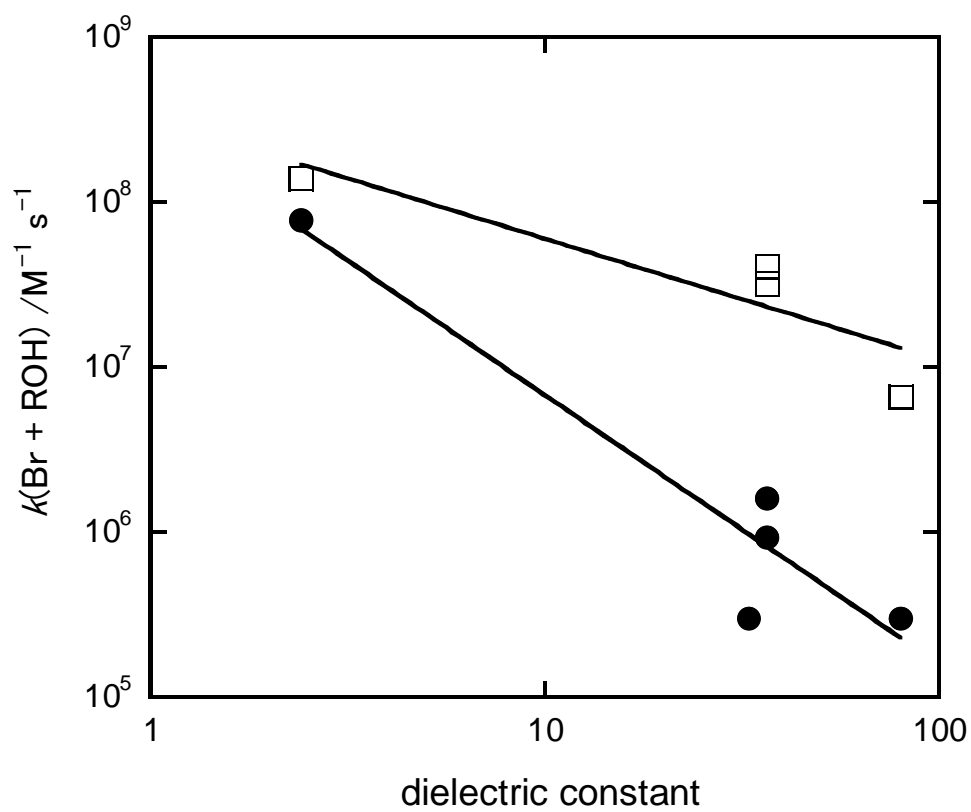Fig. 7   Sumiyoshi et al.

Fig.8 Sumiyoshi et al.
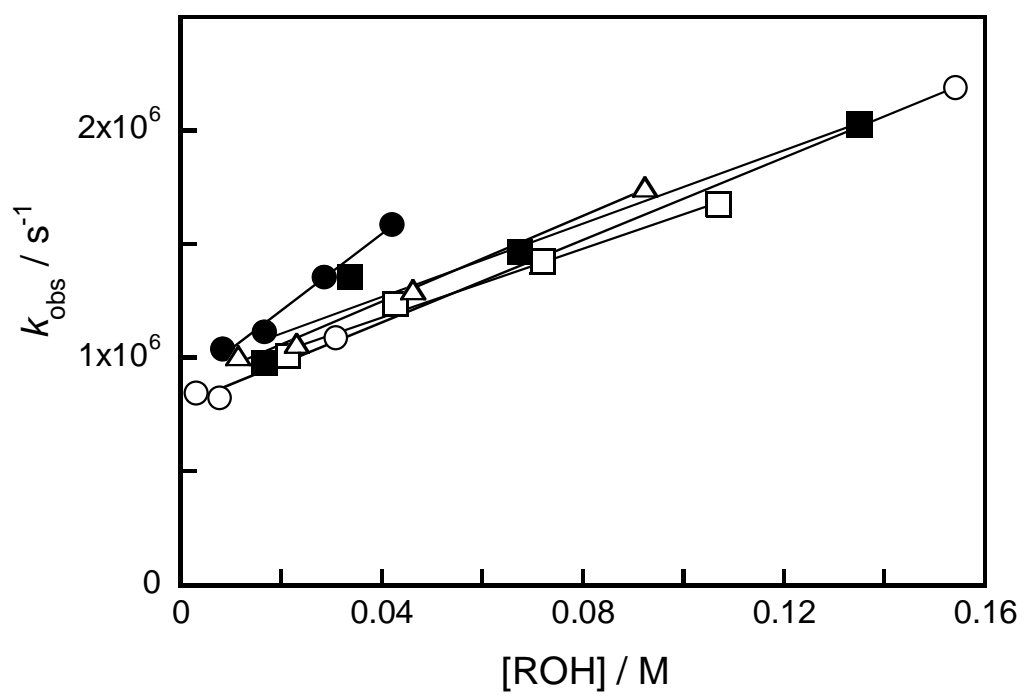
Fig.9   Sumiyoshi et al.

Fig.10   Sumiyoshi et al.

Fig.11   Sumiyoshi et al.