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Formation Mechanism of the Complexes between DMSO and Halogen Atoms. I. Pulse Radiolysis Studies

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The formation mechanism of DMSO–halogen atom complexes in the solution of DMSO and halocarbons has been investigated by pulse radiolysis method. Three formation processes have been found depending on the the solution component. In the case of DMSO/CCl_4 mixtures, the absorption band at 400 nm due to the complexes has been observed at any composition. In CCl_4 solutions, the complex is formed by the reaction of the chlorine atom with DMSO, while in DMSO solutions, the reaction between the parent radical cations of DMSO and Cl^- is dominant. It is suggested that the contribution of direct excitation of the strongly interacted ground state DMSO–CCl_4 encounter pairs becomes more important with increasing CCl_4 concentration.

We have previously reported that the irradiation of dimethyl sulfoxide (DMSO) in carbon tetrachloride results in the formation of a transient species which exhibits an absorption band at 400 nm.[1] Spectroscopic studies of the irradiated DMSO in other halocarbons such as chloroform, dichloromethane, 1,2-dichloroethane (1,2-DCE), and bromotrichloromethane have indicated the formation of DMSO–Cl complexes in the chlorinated hydrocarbons and DMSO–Br complexes in $CBrCl_3$. The kinetic study of these transient species has shown that the formation rate depends on DMSO concentrations but not on absorbed doses. In dilute DMSO solutions ($<10^{-2}$ mol dm^{-3}) it is found that the complexes are formed exclusively by the reaction of chlorine atoms with DMSO:

$$CCl_4 \rightsquigarrow CCl_4^{+}\cdot,\ Cl^-,\ CCl_3^{+}\cdot,\ CCl_3\cdot,\ Cl\cdot \text{ etc.}$$

$$\text{DMSO} + Cl\cdot \xrightarrow{k_1} \text{DMSO–Cl}. \qquad (1)$$

The bimolecular reaction rate constant, k_1, was estimated to be $(7.0\pm0.5)\times10^9$ mol^{-1} dm^3 s^{-1}.[1] The absorption of the complexes has been used as a reference system to measure the reaction rate constants of various alcohols with chlorine atoms by the competition method.[2] Quite interestingly, we found that the similar transient absorption band is formed by the pulse irradiation of CCl_4 in DMSO. However, the formation of chlorine atoms can not be expected by the radiolysis of DMSO containing small amount of CCl_4, the formation mechanism in DMSO should be different from that was observed in CCl_4 solutions. Therefore, it is interesting to elucidate the formation processes in both DMSO and CCl_4 solvents. In this paper, we report the kinetic and mechanistic studies on the formation of DMSO-halogen atom complexes produced by the pulse radiolysis of CCl_4 and CBr_4 in DMSO and DMSO in halocarbons. In addition, the formation of complexes has been also observed by the radiolysis of alkaline halides dissolved in DMSO. The possible formation mechanisms of the complexes have been discussed for DMSO/halocarbon systems and for alkaline halide in DMSO.

Experimental

Dimethyl sulfoxide and carbon tetrachloride were spectrograde (Dojin) and were used without further purification. A nanosecond pulse radiolysis system with a time resolution of 10 ns has been described eariler.[3] Electron pulses of 45 MeV and 10 ns width from an S-band linear accelerator were used as a radiation source.. The light signals were detected by a photomultiplier (Hamamatsu Photonics R928) and were accepted by a transient digitizer (Iwatsu DM901) combined with an NEC PC-9801 personal computer. The absorbed doses were measured with the KSCN dosimeter.[4] Samples were bubbled with argon in a quartz cell with an optical path length of 1 cm and sealed with a teflon bulb just before irradiation. All experiments were carried out at 18 °C.

Results and Discussion

Formation of DMSO-Cl Complexes in DMSO/CCl_4 System. Transient absorption spectra and kinetic traces have been observed in various DMSO/CCl_4 mixtures. Typical spectra obtained by the pulse radiolysis of 6.5×10^{-3} mol dm^{-3} CCl_4 in DMSO are shown in Fig. 1. The spectrum observed immediately after the pulse shows well-known features of irradiated pure DMSO.[5,6] The absorption recorded at 8 μs exhibits a maximum at 400 nm. The peak position and the shape of the spectrum is quite similar with those observed in the pulse radiolysis of DMSO dissolved in CCl_4 and other chlorinated hydrocarbons.[1] Therefore, the 400 nm band obtained in the DMSO solutions containing CCl_4 as a solute can be assigned to the DMSO–Cl complexes. Inset of Fig. 1 shows the growth and decay of the absorption at 400 nm. The pulse radiolysis studies of various DMSO/CCl_4 mixtures have been carried out to observe a spectral change depending on the DMSO/CCl_4 composition. All of the solutions show only one transient 400 nm band superimposed on the absorption spectra of irradiated pure solvents. Figure 2

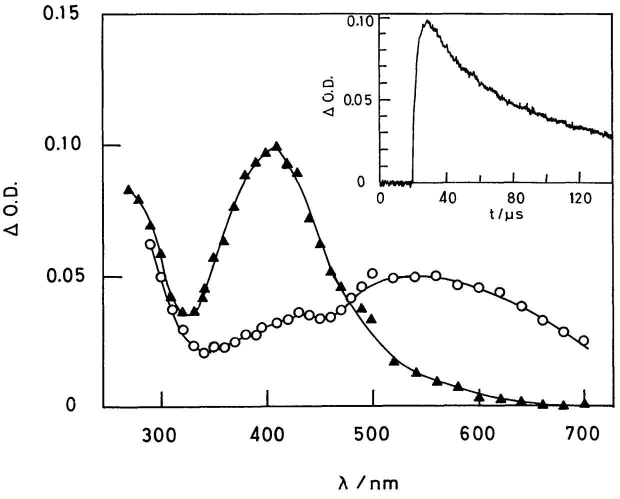

Fig. 1. Transient absorption spectra of 6.5×10^{-3} mol dm^{-3} CCl_4 in DMSO at 50 ns (○) and 8 μs (▲) after the pulse. Inset: buildup and decay of 400 nm absorption. Dose: 118 Gy.

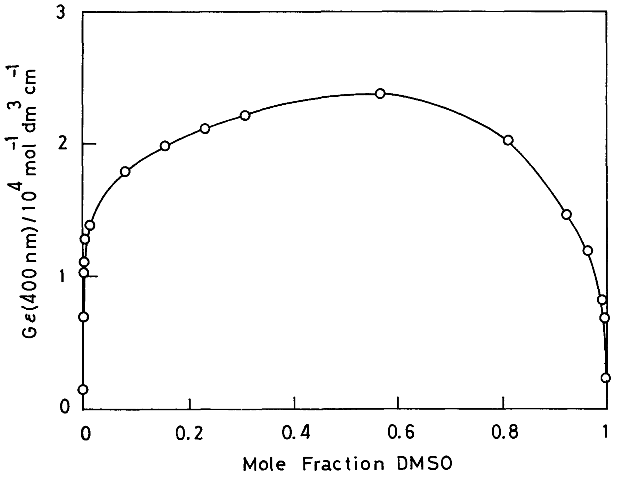

Fig. 2. Values of $G\varepsilon_{max}$ for the DMSO–Cl complex absorption band plotted against the mole fraction of DMSO in DMSO/CCl_4 mixtures.

shows the $G\varepsilon_{max}$ values of the 400 nm band obtained for each mixture as a function of solution composition. As can be seen from Fig. 2, addition of small amount of solute, DMSO or CCl_4, into the solvent, CCl_4 or DMSO, respectively, resulted in the significant increase of the 400 nm band. The maximum $G\varepsilon_{max}$ value was obtained in the mixture containing 0.6 mole fraction DMSO. The same absorption band was observed at any DMSO/CCl_4 composition, however, the formation kinetics are quite different depending on composition.

Figure 3a shows the grow-in curves of CCl_4 solutions containing a small amount of DMSO. The formation rate depends on DMSO concentrations according to a pseudo-first-order reaction ([DMSO]≫[Cl·]) by Eq. 1. On the other hand, the complexes are formed in two modes in DMSO solutions containing CCl_4. The ratio of the optical densities pertaining to the two modes depend on the concentration of solute CCl_4. The slow mode is dominant in the case of CCl_4 concentration less than 10^{-2} mol dm^{-2} and the maximum optical density increases only slightly with increasing CCl_4 concentration. While, the higher the CCl_4 concentration, the more dominant is the fast mode as shown in Fig. 3b. These results indicate that there are more than two processes for the formation of DMSO–Cl complexes in DMSO.

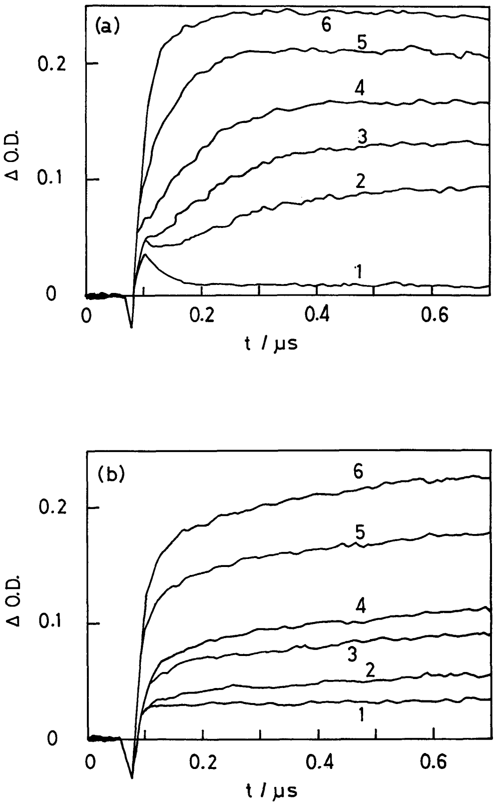

Fig. 3. Comparison of the formation kinetics of the DMSO–Cl complex at 400 nm in CCl_4 (a) and DMSO (b). (a): concentration of DMSO (in mol dm^{-3}); 1: 0; 2: 2.2×10^{-4}; 3: 4.4×10^{-4}; 4: 8.8×10^{-4}; 5: 2.2×10^{-3}; 6: 8.8×10^{-3}. (b) concentration of CCl_4 (in mol dm^{-3}); 1: 0; 2: 5.2×10^{-3}; 3: 5.2×10^{-2}; 4: 1.04×10^{-1}; 5: 5.2×10^{-1}; 6: 1.04. Dose: 135 Gy.

Formation of DMSO-Halogen Complexes in Halide/DMSO Systems. Pulse radiolysis studies revealed that solvated electrons are major direct product for the pure liquid DMSO.[5–7] Therefore, in the DMSO solutions containing CCl_4, chloride ions are produced by the dissociative electron attachment by Eq. 2:

$$e^- + CCl_4 \longrightarrow Cl^- + CCl_3\cdot . \qquad (2)$$

To understand the role of Cl^- ions in the formation of the complexes, alkaline halides such as KCl and $CaCl_2$

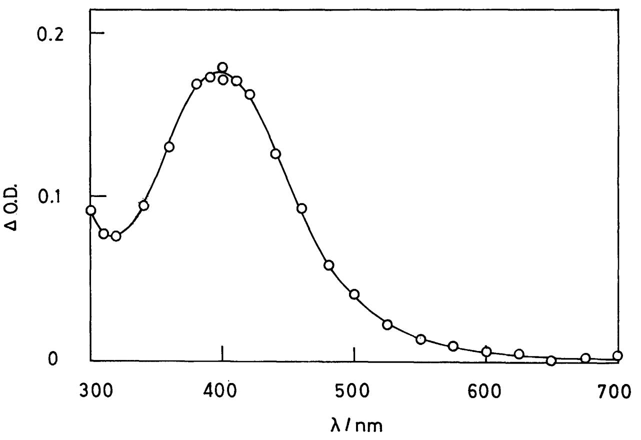

Fig. 4. Absorption spectrum observed at 200 ns after the pulse radiolysis of 8.8×10^{-3} mol dm^{-3} KCl in DMSO. Dose: 172 Gy.

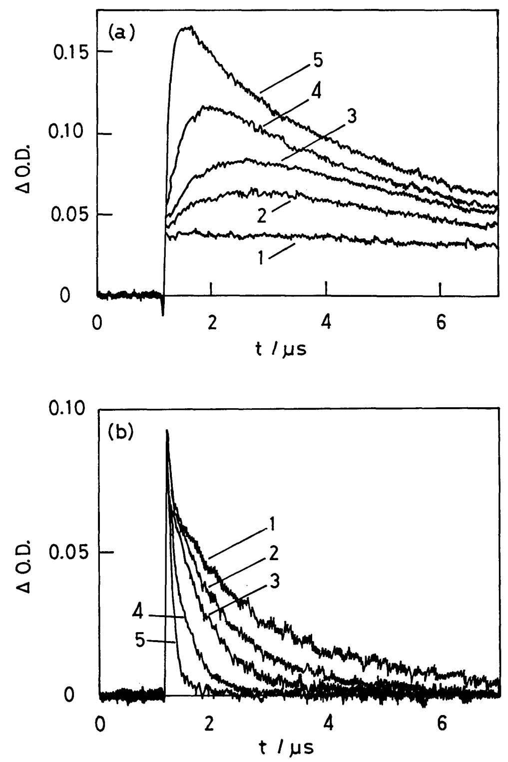

Fig. 5. Effect of concentration of KCl on the transient absorption. (a), 400 nm; (b), 600 nm. Concentration of KCl (in mol dm^{-3}); 1: 0; 2: 6.47×10^{-5}; 3: 1.42×10^{-4}; 4: 4.96×10^{-4}; 5: 2.48×10^{-3}. Dose 185 Gy.

were dissolved and pulse irradiated in DMSO. Figure 4 shows the absorption spectrum obtained at 200 ns after the pulse radiolysis of 8.8×10^{-3} mol dm^{-3} KCl in DMSO. The peak position and the spectral shape are quite similar to those obtained in DMSO/CCl_4 systems. Therefore, this 400 nm band can be attributed to the DMSO–Cl complexes. The grow-in traces at 400 nm are shown in Fig. 5a. The grow-in rate and the maximum optical density increase with increasing KCl concentration. Figure 5b shows the dependence of the decay traces at 600 nm on the concentration of KCl. The decay rates follow a first-order-kinetics and increase as the KCl concentration increases. The same kinetic behavior was observed in the case of the irradiated $CaCl_2$ in DMSO. The increase of the grow-in rate at 400 nm with increasing Cl^- concentrations in accordance with the increase of the decay rate at 600 nm strongly indicates that the Cl^- ions react with transients with an absorption maximum at around 550 nm produced by the radiolysis of pure DMSO, leading to the species with an absorption maximum at 400 nm.

Radiolysis of DMSO has been studied extensively by many researchers.[5–10] On the pulse irradiation of pure DMSO a transient species absorbing at 600 nm was obtained, which is due to either the parent radical cation, $(CH_3)_2SO^{+\cdot}$ or some radical derived therefrom.[6,7] Irradiation of the pure DMSO at low temperatures gave ESR features for methyl radicals, formed by dissociative electron capture together with a species tentatively identified as the radical cation or its dimer.[8] However, well defined ESR features were obtained for the parent cation using $CFCl_3$ as a solvent, which had an intense violet color, indicative of an absorption band in the 550 nm region.[9] Therefore, the present experimental results strongly suggest that the reaction of parent radical cations of DMSO with the chloride ions results in the DMSO–Cl complex formation:

$$\mathrm{DMSO} \rightsquigarrow \mathrm{DMSO}^{+\cdot} + e^- \tag{3}$$

$$\mathrm{DMSO}^{+\cdot} + \mathrm{Cl}^- \longrightarrow \mathrm{DMSO{-}Cl}. \tag{4}$$

For the DMSO solutions containing CCl_4, the expected amount of Cl^- ions produced on irradiation can be estimated using the reported free ion yield of DMSO, $G(\text{free ion})=1.8$,[6] to be 2.5×10^{-5} mol dm^{-3} at 135 Gy (Fig. 3b). This concentration can be enough to produce a significant amount of complexes based on the results shown in Fig. 5a. Therefore, the slow formation process observed for the low concentration CCl_4 in DMSO can be attributed to reaction 4.

Other halide ions, Br^- and I^-, and a pseudo-halide ion, SCN^- also react with DMSO radical cations. The bimolecular rate constants for reaction 4 were measured from the pseudo-first-order decay of the optical density at 600 nm for 5×10^{-5}—1.5×10^{-3} mol dm^{-3} X^-(X=Cl, Br, I, SCN) as illustrated in Fig. 6. The obtained rate constants and the absorption maximum of the complexes are given in Table 1.

In the case of Cl^-, only the transient absorption spectrum of DMSO–Cl complexes was observed at any concentration. On the other hand, in the case of Br^- the transient spectra depend on the concentration as

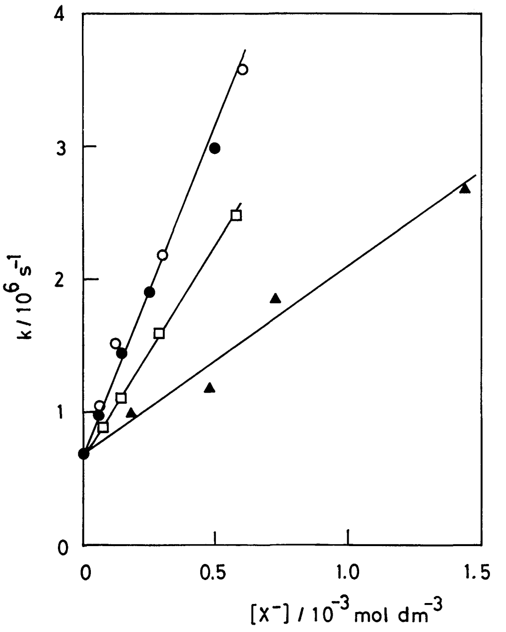

Fig. 6. Apparent reaction rate constants of the decay of 600 nm band. ●: Cl^-; ○: Br^-; □: I^-; ▲: SCN^-.

Table 1. Bimolecular Rate Constants of the Reaction of $DMSO^{+\cdot}$ with Cl^-, Br^-, I^-, and SCN^- and the Absorption Maxima of the Complexes in DMSO

X^-	$k/10^9\ mol^{-1}\ dm^3\ s^{-1}$	λ_{max}/nm
Cl^-	5.0	400
Br^-	5.0	430
I^-	3.2	—
SCN^-	1.4	—

shown in Fig. 7. For dilute solution of Br^- ($<10^{-3}$ mol dm^{-3}), only the transient spectra of the DMSO–Br complexes with a maximum at 430 nm were observed, while at relatively high concentration of Br^- (1.33×10^{-3} mol dm^{-3}), the formation of the complex band is followed by the conversion into a 360 nm band which can be assigned to Br_2^-.[11] Since such conversion has not been observed in the case of the irradiation of CBr_4 in DMSO, the reaction of DMSO–Br complexes with Br^- must be responsible for the formation of Br_2^-:

$$\mathrm{DMSO\text{-}Br + Br^- \longrightarrow DMSO + Br_2^-.} \qquad (5)$$

And further conversion from 360 to 280 nm band was observed at higher Br^- concentration ($>10^{-2}$ mol dm^{-3}) which can be due to Br_3^-:[11]

$$\mathrm{Br_2^- + Br_2^- \longrightarrow Br_3^- + Br^-.} \qquad (6)$$

The distinguishable transient absorption spectra of the DMSO–X complexes have not been obtained for I^- and SCN^- probably due to the short lifetime of the complexes and the spectral overlap with those of the pure solvent. Instead of those, well-known spectra of I_2^- [12] and $(SCN)_2^-$ [13] were observed to build-up after the pulse even in the dilute solutions.

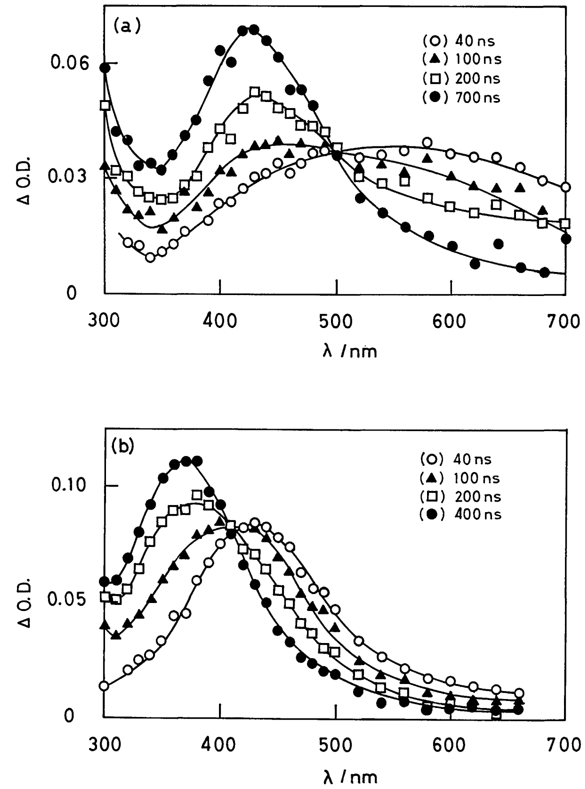

Fig. 7. Transient absorption spectra obtained after the pulse radiolysis of NaBr in DMSO. (a) 5.32×10^{-4}; (b) 1.33×10^{-3} mol dm^{-3} NaBr. Dose: 103 Gy.

Fast Formation Mode of Complexes in DMSO. The fast mode of complex formation observed for the high concentration CCl_4 ($>10^{-2}$ mol dm^{-3}) in DMSO can be due to the direct excitation of the ground state DMSO–CCl_4 associated pairs. The ability of complex formation of DMSO with various compounds has been well-known.[14] The relatively large dipole moment of DMSO as well as the behavior of the enthalpy of mixing and excess viscosity of the system DMSO/CCl_4 suggest that both, DMSO–DMSO as well as DMSO–CCl_4 associations, are present.[15] The ground state molecules of both DMSO and CCl_4 absorb below 250 nm very strongly, while the absorption edge of DMSO/CCl_4 mixtures shifts towards red. These experimental results suggest the direct excitation mode contributes to the complex formation:

$$\mathrm{DMSO\text{-}CCl_4 \xrightarrow{h\nu} DMSO\text{-}Cl.} \qquad (7)$$

Further evidence of the direct excitation of the ground state DMSO–CCl_4 association pairs by laser flash photolysis leading to the complex formation will be

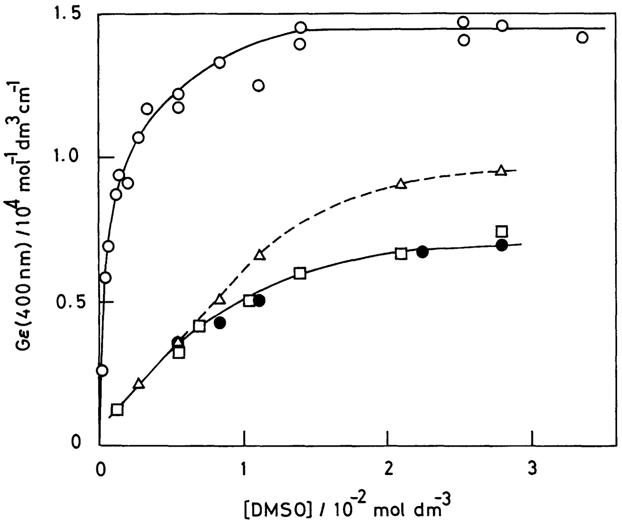

Fig. 8. Effect of DMSO concentration on the yield of DMSO-Cl complexes in halocarbons. (○), CCl_4; (□), $CHCl_3$; (△), CH_2Cl_2; (●), 1,2-DCE.

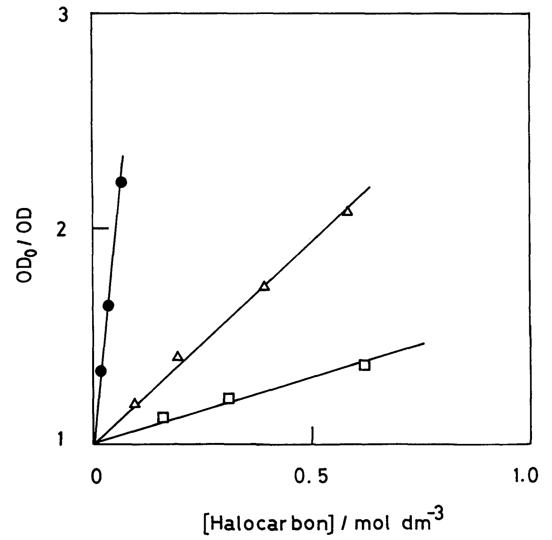

Fig. 9. Competition between DMSO and halocarbons for chlorine atoms in CCl_4. (□), $CHCl_3$; (△), CH_2Cl_2; (●), 1,2-DCE. [DMSO]=2.8×10^{-3} mol dm^{-3}.

given in the forthcoming paper.

Formation of DMSO-Cl Complexes in Other Halocarbons. Figure 8 shows the effect of DMSO concentrations on the yield ($G\varepsilon_{max}$) of the DMSO-Cl complex in CCl_4, $CHCl_3$, CH_2Cl_2, and 1,2-DCE. As can be seen from Fig. 8 the yield of the complex in CCl_4 rises sharply as the concentration of DMSO increases and reaches a pleatue value at 1.5×10^{-2} mol dm^{-3} DMSO. On the other hand, the yields of the complex in other halocarbons rise slowly. This difference indicates the existence of the competitive reactions for the chlorine atoms, i.e., hydrogen abstraction reactions from halocarbons, for example:

Table 2. Reaction Rate Constants of Chlorine Atoms with $CHCl_3$, CH_2Cl_2 and 1,2-DCE in CCl_4

Halocarbon	$k/10^7$ mol^{-1} dm^3 s^{-1}
$CHCl_3$	1.2
CH_2Cl_2	3.7
1,2-DCE	37

$$CHCl_3 + Cl\cdot \longrightarrow CCl_3\cdot + HCl. \qquad (8)$$

The reaction rate constants of the chlorine atoms with halocarbons have been measured by the competitive kinetic method.[2] Various amount of halocarbons was added to 2.8×10^{-3} mol dm^{-3} DMSO in CCl_4, and the ratio of the optical absorption at 400 nm in the absence and presence of halocarbons was plotted against DMSO concentrations. From the slopes of the straight lines shown in Fig. 9 the reaction rate constants of chlorine atoms with halocarbons were calculated and given in Table 2. The reaction rate constants are 1/20—1/600 of that of the chlorine atoms with DMSO. Quite different reaction rate constants of the reaction between chloroform and chlorine atoms have been reported, 10^7 mol^{-1} dm^3 s^{-1} by Russel et al.[16] and 6×10^4 mol^{-1} dm^3 s^{-1} by Bibler.[17] The former value is in good agreement with the present experimental result, 1.2×10^7 mol^{-1} dm^3 s^{-1}.

Conclusion

The pulse radiolysis of DMSO/CCl_4 system and alkaline halides in DMSO has provided evidence of three different DMSO-halogen atom complex formation routes. In CCl_4 solutions, the reaction of the chlorine atoms with DMSO is the main route. On the other hand, in DMSO media containing alkaline chlorides or low concentration of CCl_4, the reaction of DMSO parent radical cations with chloride ions is dominant and the contribution of the direct excitation of the ground state DMSO-CCl_4 associated pairs becomes more important as CCl_4 concentration increases.

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