Formation Mechanism of the Complexes between DMSO and Halogen Atoms. II. Laser Flash Photolysis Studies

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The laser flash photolysis of DMSO/CCl_4 mixed solutions produces the transient DMSO-Cl complex with an absorption maximum at 400 nm. The formation of the complex has been explained by the direct photoexcitation of the ground state associated DMSO/CCl_4 pair on the basis of the spectroscopic data and the known macroscopic physical properties of binary solutions of DMSO and CCl_4.

Recently, Sumiyoshi and Katayama have reported that the pulse radiolysis of DMSO (=dimethyl sulfoxide) in CCl_4[1] and CCl_4 in DMSO[2] results in the formation of a transient DMSO-Cl complex with an absorption maximum at 400 nm. In CCl_4 and other chlorinated hydrocarbons kinetic and spectroscopic studies have indicated the formation mechanism of DMSO-Cl complexes exclusively via the reaction of chlorine atoms with DMSO:

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

The bimolecular reaction rate constant, k_1, was estimated to be $(7.0\pm0.5)\times10^9$ $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$.[1] On the other hand, the complexes are formed in two modes in DMSO solutions containing CCl_4.[2] The ratio of the optical densities pertaining to the two modes depends on the concentration of solute CCl_4. The slow mode is dominant in the case of CCl_4 concentration less than 10^{-2} $\mathrm{mol\,dm^{-3}}$. While, the higher the CCl_4 concentration, the more dominant is the fast mode. These results indicate that there are more than two routes for the formation of DMSO-Cl complexes in DMSO. The slow mode has been ascribed to the reaction of parent radical cations of DMSO with cloride ions based on the results obtained in the pulse radiolysis experiments of alkaline chlorides in DMSO:

$$\mathrm{DMSO} \rightsquigarrow \mathrm{DMSO}^{+\cdot} + \mathrm{e}^-, \qquad (2)$$

$$\mathrm{e}^- + \mathrm{CCl_4} \longrightarrow \mathrm{Cl}^- + \mathrm{CCl_3}\cdot, \qquad (3)$$

$$\mathrm{DMSO}^{+\cdot} + \mathrm{Cl}^- \xrightarrow{k_2} \mathrm{DMSO\text{-}Cl}. \qquad (4)$$

The rate constant for the reaction 4 was estimated to be $k_2=5.0\times10^9$ $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ in the pulse radiolysis study of chloride ions in DMSO.[2] The fast mode has been tentatively attributed to the direct excitation of the ground state DMSO/CCl_4 associated pairs. The laser flash photolysis experiments reported in this paper were undertaken in order to address the question of direct excitation of the DMSO/CCl_4 associated pair leading to the formation of the DMSO-Cl complex.

Experimental

Dimethyl sulfoxide and carbon tetrachloride were spectrograde (Dojin) and were used without further purification. UV-Vis spectra of the mixed solutions were recorded with a Hitachi U-3200 spectrophotometer.

Laser flash photolysis experiments were performed using a Quanta-Ray DCR-11 Nd: YAG laser operated in combination with two frequency doublers (KD*P and BBO) as the excitation pulse (266 nm), and a 1 kW Xe lamp as the probe light. The duration of the laser pulse was 6 ns (half width). Actinometry was performed with an aqueous solution of 4.5×10^{-5} $\mathrm{mol\,dm^{-3}}$ $K_4[Fe(CN)_6]$ ($\Phi(e_{aq}^-)=0.51$ at 266 nm).[3] The maximum laser output at $\lambda=266$ nm was estimated to be 6.9×10^{15} photons per flash. The light signals were detected by a photomultiplier (Hamamatsu Photonics R928) through a monochromator (Shimadzu Bausch and Lomb) and were accumulated by a transient digitizer (Iwatsu DM901) with the shortest resolvable time of 10 ns combined with an NEC PC 9801 personal computer. 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 photolysis. All experiments were carried out at 18 °C.

Results and Discussion

Both DMSO and CCl_4 absorb light below 270 nm strongly. The transmittance at 266 nm is 26 and 30 % for DMSO and CCl_4 respectively. On mixing of DMSO and CCl_4 the optical absorption of the solution shifts toward red. Figure 1 shows the effect of composition on the wavelength at 50 % transmittance. The wavelength at 50 % transmittance of the mixed solutions shifts as much as 30 nm. These results indicate the existence of the strong interaction between DMSO and CCl_4 molecules over a wide range of CCl_4 concentrations. The increase of the wavelength at 50 % transmittance in the range pure CCl_4 to 0.1 mole fraction DMSO is not so sharp as that in the range pure DMSO to 0.9 mole fraction DMSO. This difference should be due to the predominant dimer formation of DMSO in the concentration range 0.02—0.3 $\mathrm{mol\,dm^{-3}}$ DMSO as indicated by the infrared studies.[4]

The association phenomena of DMSO with polariz-

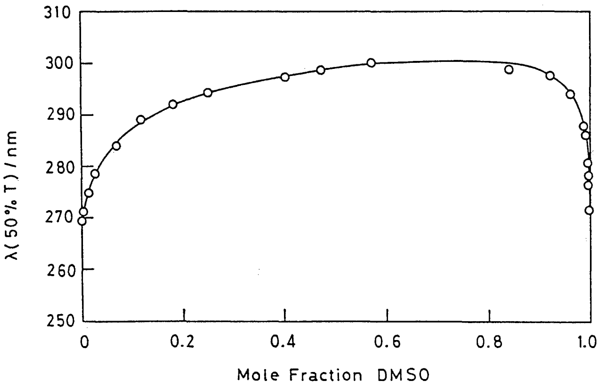

Fig. 1. Dependence of the wavelength at 50% transmittance on the mole fraction DMSO in DMSO/CCl_4 mixtures.

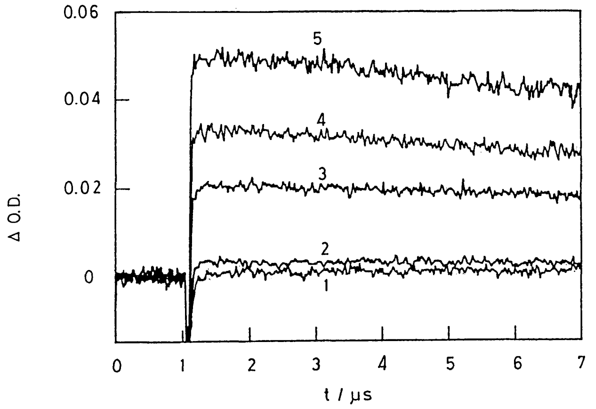

Fig. 3. Transient changes in optical absorption at 400 nm following the pulsed laser excitation (266 nm) of CCl_4 in DMSO: (1) pure DMSO; (2) pure CCl_4; (3) 1.3×10^{-2}; (4) 1.95×10^{-2}, (5) 2.6×10^{-2} mol dm^{-3} CCl_4 in DMSO.

able and polar neutral molecules as well as ionic species have been reviewed previously by Szmert.5) In the case of DMSO and CCl_4 mixtures, thermodynamic data suggest a marked interaction between these species. Later, intermolecular interaction between DMSO and CCl_4 has been suggested by the studies of IR spectroscopy,6) and surface tension, viscosity and refractive index.7) Both association of DMSO with CCl_4 as well as self association of DMSO have been suggested based on the relatively large dipole moment, the positive mixing enthalpy and the relatively slow rotational and translational motion in the limit of high dilution in CCl_4.8)

Figure 2 shows the transient absorption spectra of 1.95×10^{-2} mol dm^{-3} CCl_4 in DMSO observed immediately after the 266 nm photolysis. Similar spectra with an absorption maximum at 400 nm have been obtained for dilute DMSO ($<1.4\times10^{-1}$ mol dm^{-3}) in CCl_4. The peak position and the shape of the spectrum are quite similar with those obtained in the pulse radiolysis of DMSO in $CCl_4$1) and CCl_4 in DMSO.2) The 400 nm band intensity decays by the second order kinetics as observed in the pulse radiolysis of DMSO/CCl_4 system. Therefore, the 400 nm band obtained by the 266 nm photolysis of DMSO/CCl_4 can be assigned to the DMSO-Cl complex.

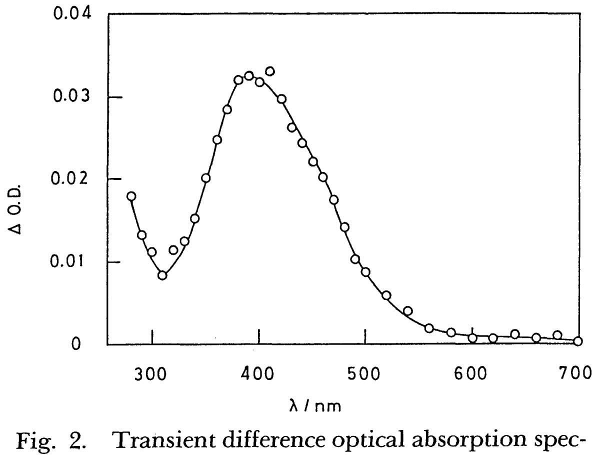

Fig. 2. Transient difference optical absorption spectrum recorded immediately after the pulsed laser excitation (266 nm) of 1.95×10^{-2} mol dm^{-3} CCl_4 in DMSO.

Figure 3 shows the time profile of the absorbance at 400 nm for various CCl_4 concentration and pure solvents. Both pure CCl_4 and DMSO exhibit very small transient absorption at 400 nm. Experiments are limited to the low concentration CCl_4 ($<3\times10^{-2}$ mol dm^{-3}) solutions in DMSO due to the strong absorption of the mixed solutions at 266 nm. However, the present results show increasing formation of the complex band with increasing CCl_4 concentration in DMSO. The 400 nm band is formed only during the laser pulse even for low concentration CCl_4 (6.5×10^{-3} mol dm^{-3}). Quite similar kinetic data have also been obtained in the present laser photolysis experiment of DMSO (2.8×10^{-3}—1.4×10^{-1} mol dm^{-3}) in CCl_4. These results indicate that the formation of the complex must be the consequence of excitation of the ground state associated DMSO/CCl_4 pairs, but not the reaction of excited DMSO or CCl_4:

$$(\mathrm{DMSO}\cdots\mathrm{CCl_4}) \xrightarrow{h\nu} \mathrm{DMSO\text{-}Cl}. \qquad (5)$$

Comparison of the present results with those observed in the pulse radiolysis is quite interesting. The pulse radiolysis of dilute DMSO in CCl_4 shows a first order grow-in kinetics of the complex formation, that is, the rate depending on the DMSO concentration.1) On the other hand, the irradiation of dilute CCl_4 in DMSO shows a slow formation process up to several microseconds.2) The former has been attributed to the reaction of chlorine atoms with DMSO and the latter to the reaction of the parent DMSO cation with cloride ions. The latter process is found to be superimposed on the fast formation process which becomes more dominant as the CCl_4 concentration increases. This fast formation process is understood to be a direct excitation route of the associated DMSO/CCl_4 pair as is evidenced in the present laser flash photolysis experiments.

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