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# Pulse Radiolysis-Laser Flash Photolysis Studies of Diphenyl Sulfide in Liquid Halocarbons

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The combined pulse radiolysis-laser flash photolysis method has established that the excited state of diphenyl sulfide/chlorine atom complexes readily undergoes intermolecular hydrogen abstraction, while the excited state of diphenyl sulfide/bromine complexes is de-excited without any reactions.

Due to their high ionization potential, halocarbons have been used as useful solvents to study solute cations.1) Irradiation of halocarbon solutions produces arene/halogen atom complexes2) and dimethyl sulfoxide/halogen atom complexes.3) Although the spectra4) and reactivities5) of these complexes have been studied extensively, the nature of the excited complexes has not been extensively studied. In this letter we report the reaction of diphenyl sulfide (DPS)/halogen atom (Cl and Br) complexes in the excited state.

The complexes were produced upon irradiation of solutions by a pulsed electron beam from an S-band linear electron accelerator (45 MeV and 10 ns half-width). An Nd:YAG laser (Quanta-Ray, DCR-11) was used as the excitation source. Excitation of the transient complexes was carried out at 355 nm (<60 mJ/pulse) and 532 nm (<50 mJ/pulse). Solutions in a 10 x 10 x 40 mm$^3$ rectangular quartz cell were deaerated by a stream of argon and sealed with a teflon valve. The electron beam and the laser beam were focused to a 3 mm diameter spot. A parallel beam arrangement was applied to the electron beam and laser beam. The analyzing light from a 1 kW xenon arc lamp illuminated the cell perpendicular to both electron and laser beams. Transient spectra and kinetic traces were obtained by a convepntional photomultiplier system. All studies reported were carried out at room temperature (18-20°C).

The transient spectra obtained 100 ns after pulse radiolysis of $10^{-3}$ and $10^{-1}$ mol dm$^{-3}$ DPS in 1,2-dichloroethane and 3 x $10^{-3}$ mol dm$^{-3}$ DPS in $CBrCl_3$ are shown in Fig. 1. The 780 nm band observed in 1,2-dichloroethane is assigned to the diphenyl sulfide radical cation, based on the previous result obtained by $\gamma$-radiolysis of DPS in halocarbon matrices at 77 K.[1] The intensity decayed with 2nd order kinetics (Fig. 1. inset), independent of concentration of DPS. The 340 and 520 nm bands become more intense as the DPS concentration increases (Fig. 1. A). The lifetimes of these bands were identical, which implies that these two bands are related to a single transient species. These typical UV-vis bands were also observed in dichloromethane (340 and 540 nm), carbon tetrachloride (340 and 505 nm) and $CBrCl_3$ (350 and 530 nm) as well. These bands are assigned to $\pi$-complexes of DPS with a halogen atom, based on the similarity of the band position and spectral shape of various arene/Cl $\pi$-complexes[4]. Rate constants of 1–2 x $10^{10}$ mol$^{-1}$ dm$^{3}$ s$^{-1}$ were obtained in carbon tetrachloride and 1,2-dichloroethane, applying the halflife time of chlorine atoms, 140 ns[6] and 8 ns[7] respectively.

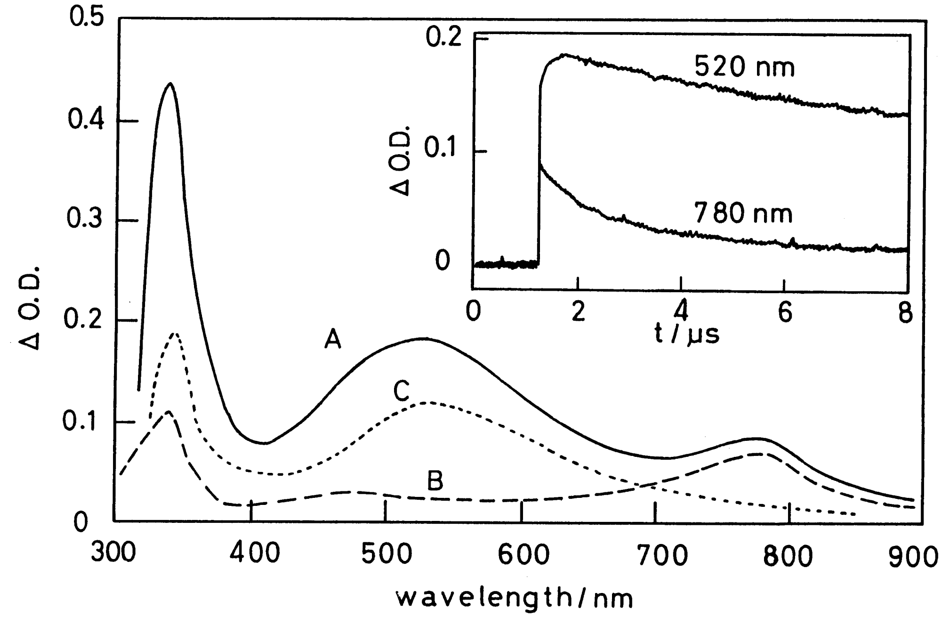

Fig. 1. Transient absorption spectra obtained 100 ns after electron pulse irradiation of $10^{-1}$ (A) and $10^{-3}$ (B) mol dm$^{-3}$ DPS in 1,2-dichloroethane and 3 x $10^{-3}$ mol dm$^{-3}$ DPS in $CBrCl_3$ (C).
Inset: decay traces for $10^{-1}$ mol dm$^{-3}$ DPS in 1,2-dichloroethane at 520 and 780 nm.

In 1,2-dichloroethane and dichloromethane, successive irradiation by an electron beam and a laser pulse caused photobleaching of the complex bands, as illustrated in Fig. 2. Photobleaching was induced by laser excitation at both 355 and 532 nm and was completed within 10 ns, which is the resolution time of the present experiment. The degree of photobleaching was proportional to the laser intensity, indicating a one-photon process. On the contrary, photobleaching was not observed for DPS/Cl complexes in carbon tetrachloride and for DPS/Br complexes in $CBrCl_3$. In $CCl_4$, since no photobleaching was observed in the DPS concentration range examined up to 0.3 mol $dm^{-3}$, the reaction of the excited DPS/Cl complexes with solute DPS is inefficient. However, upon addition of hydrogen containing solutes (such as dichloromethane, cyclohexane, and 2-methyl-2-propanol) to the $CCl_4$ solutions, photobleaching was observed as illustrated in Fig. 3. The decrease of the initial optical density is due to the competitive reaction between DPS and additives towards chlorine atoms. The previously determined rate constants are $k$(dichloromethane + Cl) = 3.7 x $10^7$,$^{3)}$ $k$(cyclohexane + Cl) = 6 x $10^9$,$^{8)}$ and $k$(2-methyl-2-propanol + Cl) = 3.2 x $10^9$ $mol^{-1}$ $dm^3$ $s^{-1}$.$^{6)}$

On the other hand, DPS/Br complexes in $CBrCl_3$ were not affected by the addition of hydrogen containing solutes (Fig. 4), indicating that excited DPS/Br complexes do not undergo hydrogen abstraction. The difference in

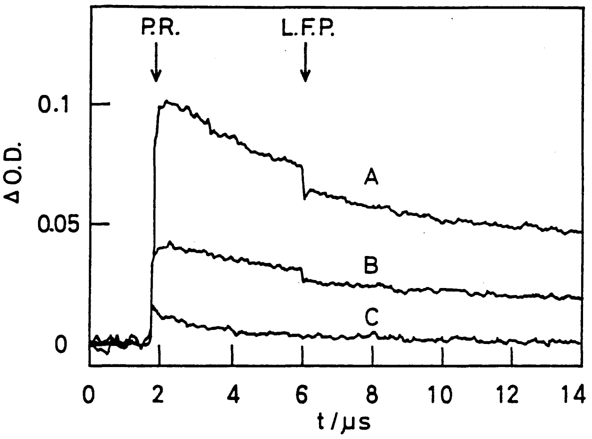

Fig. 2. Combined pulse radiolysis (P.R.) and laser flash photolysis (L.F.P). 0.3 mol $dm^{-3}$ DPS in 1,2-dichloroethane.
$\lambda_{ex}$=532 nm.
$\lambda_{obsd}$ (A) 340 nm
(B) 500 nm
(C) 790 nm

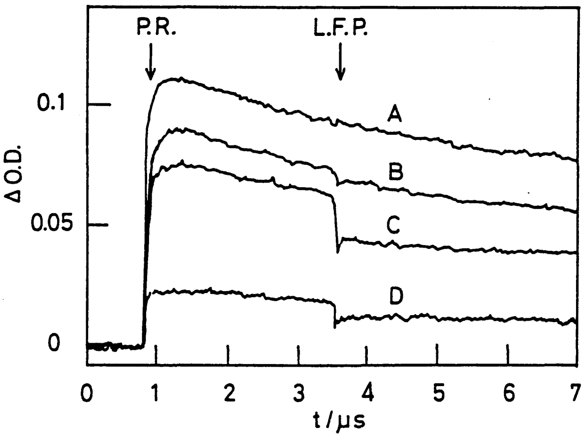

Fig. 3. Effects of additives on the reaction of the excited DPS/Cl complex in $CCl_4$ (3 x $10^{-2}$ M DPS).
$\lambda_{ex}$=532 nm. $\lambda_{obsd}$=340 nm.
(A) no additive
(B) 1.6 mol $dm^{-3}$ dichloromethane
(C) 0.92 mol $dm^{-3}$ cyclohexane
(D) 1.1 mol $dm^{-3}$ 2-methyl-2-propanol

reactvities of the excited states can be attributed to the reactities of chlorine atoms and bromine atoms. Hydrogen abstraction by chlorine atoms is exothermic; on the other hand hydrogen abstraction by bromine atoms is endothermic.[9] Present results demonstrate that reactions of the excited diphenyl sulfide/chlorine and bromine complexes are fast processes in which intermolecular hydrogen abstraction occurs predominantly in the presence of chlorine complexes, while deactivation occurs exclusively with the bromine complexes. The reactions are summarized in the following schemes.

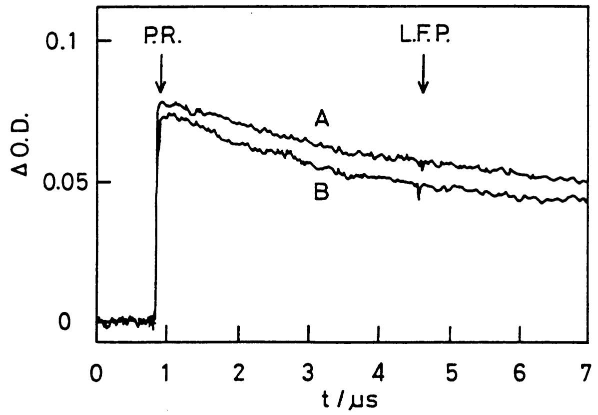

Fig. 4. Pulse radiolysis and laser flash photolysis of $3 \times 10^{-3}$ M DPS in $CBrCl_3$. $\lambda_{ex}=532$ nm. $\lambda_{obsd}=560$ nm.
(A) no additive
(B) 0.46 mol $dm^{-3}$ cyclohexane

$$\mathrm{DPS} + \mathrm{Cl}^{\cdot} \longrightarrow (\mathrm{DPS/Cl}^{\cdot}) \overset{h\nu}{\rightleftharpoons} (\mathrm{DPS/Cl}^{\cdot})^{*} \xrightarrow{\mathrm{RH}} \mathrm{DPS} + \mathrm{HCl}$$

Scheme 1.

$$\mathrm{DPS} + \mathrm{Br}^{\cdot} \longrightarrow (\mathrm{DPS/Br}^{\cdot}) \overset{h\nu}{\rightleftharpoons} (\mathrm{DPS/Br}^{\cdot})^{*} \xrightarrow{\mathrm{RH}} \mathrm{DPS} + \mathrm{HBr}$$

Scheme 2.

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