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Photochemistry of Diphenyl Sulfide/Halogen and Mesitylene/Halogen Complexes in Liquid Halocarbons

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(Received April 9, 1993)

The photochemical reactions of the diphenyl sulfide/X (X=Cl, Br) and mesitylene/X complexes have been studied by the combined pulse radiolysis–laser flash photolysis method. While no photochemistry is observed from the excited state of diphenyl sulfide/Cl complexes in CCl_4, permanent photobleaching induced by intermolecular hydrogen abstraction is observed in 1,2-dichloroethane ($\Phi=0.05$) and in CCl_4 which contains an additive such as dichloromethane, cyclohexane, and 2-methyl-2-propanol. The excited state of mesitylene/Cl complexes undergoes solvent independent intramolecular hydrogen abstraction with a quantum yield of 0.10. No photochemistry is observed from the excited states of diphenyl sulfide/Br and mesitylene/Br complexes in $CBrCl_3$ with and without containing cyclohexane. The difference in the bond dissociation energy of H–Cl, H–Br, and C–H explains the dependence of the photochemical reaction modes on both solvents and halogens.

Both pulse radiolysis and laser flash photolysis techniques have been contributing to the understanding of reactions of short-lived transients such as the excited states and radical ions. Recently, a combination of these two fast kinetic methods has made possible investigations on reactions of excited states of transient ionic species(1) and of radicals,(2) and reactions of excited states with radicals.(3)

In our previous paper,(4) we studied the photochemistry of diphenyl sulfide (DPS)/Cl and DPS/Br complexes. Nature of photochemical reactions depends on solvents and the counter-halogen atoms. Permanent photobleaching was observed for DPS/Cl complexes in 1,2-dichloroethane but not in CCl_4. The photobleaching of the Cl complexes was attributed to intermolecular hydrogen abstraction based on effects of additives to the CCl_4 solutions. No photobleaching was observed for DPS/Br complexes in $CBrCl_3$. In this paper we report more detailed results including mesitylene/Cl and Br π-complexes in liquid halocarbons. Although the spectra(5) and reactivities(6) of various arene/halogen π-complexes have been studied extensively, the reactions of the excited π-complexes have not been reported so far.

Experimental

Materials. Bromotrichloromethane ($CBrCl_3$) from Wako was distilled under nitrogen flow. 1,2-Dichloroethane, dichloromethane, carbon tetrachloride, benzene, cyclohexane (spectral grade), and naphthalene (scintillation grade) from Dojin were used as received. Diphenyl sulfide, mesitylene, 2-methyl-2-propanol, and benzophenone (special guaranteed reagent grade) from Wako were used without further purification.

Irradiation. The complexes were produced upon irradiation of halocarbon solutions by a pulsed electron beam (45 MeV and 10 ns half-width) from an S-band linear electron accelerator. Excitation of the transient complexes was carried out with a second harmonic pulse at 532 nm or a third harmonic pulse at 355 nm (6 ns pulse width) from an Nd:YAG laser (Quanta-Ray, DCR-11). Solutions in a $10\times10\times40$ mm^3 rectangular quartz cell were deaerated by a stream of argon and sealed with a Teflon valve. The electron and laser beam were collinearly focused to a 3 mm diameter spot. The analyzing light from a 1 kW xenon arc lamp illuminated the cell perpendicularly to both electron and laser beams. Transient spectra and kinetic traces were obtained by a conventional photomultiplier system. Further details of the pulse radiolysis setup have been described previously.(7) All measurements were carried out at room temperature (18—20 °C).

Actinometry. To estimate the number of incident laser photons at $\lambda_{ex}=355$ nm, benzene solutions containing benzophenone (1×10^{-3} mol dm^{-3}) and naphthalene (1×10^{-1} mol dm^{-3}) were used as an actinometer. The optical absorption of the naphthalene triplets formed by energy transfer from the benzophenone triplets was measured ($\varepsilon_{425\ nm}=1.32\times10^4$ dm^3 mol^{-1} cm^{-1},(8) $\Phi=1.0$(9))). N_2O saturated KSCN aqueous solutions (10^{-3} mol dm^{-3}) were used to determine the number of incident photons at $\lambda_{ex}=532$ nm. The quantum yield of 0.07 for the dissociation of $(SCN)_2^-$ to $SCN+SCN^-$ and the extinction coefficients of $(SCN)_2^-$ were taken from the literature.(10) Terephthalate aqueous solutions (10^{-4} mol dm^{-3}) were also used as an actinometer. The photoionization of terephthalate anions was induced by the 355 and 532 nm light. The reported quantum yields for photoionization of terephthalate anions, $\Phi=0.05$ at 365 nm, and $\Phi=0.07$ at 520 nm, were used for 355 and 532 nm excitation, respectively.(11) Numbers of the incident photons determined were in good agreement with values obtained by the two different actinometers at each wavelength.

Extinction Coefficients of the Complexes. The extinction coefficients of the transient complexes were determined relative to that of the benzene/Cl complex, i.e., 1800 dm^3 mol^{-1} cm^{-1} at 490 nm in benzene.(12) Assuming the extinction coefficient for benzene/Cl π-complexes is identical in benzene and CCl_4, we obtained the radiation chemical yield of the benzene/Cl π-complexes in CCl_4 as 0.17 μmol J^{-1} (1.6 molecules/100 eV) at the infinite benzene concentration. Assuming the same yield of π-complexes for DPS/Cl and mesitylene/Cl in CCl_4, the extinction coefficients were estimated from the linear plots of OD^{-1} vs. inverse solute concentrations. Thus, the extinction coefficients were determined as follows: 12900 (340 nm), 9200 (355 nm), and 5700 (520 nm) for DPS/Cl complexes, 7300 (300 nm), 3700 $dm^3 mol^{-1} cm^{-1}$ (355 nm) for mesitylene/Cl complexes. We assumed that the extinction coefficients are unchanged at the peak wavelengths in CCl_4 and other halocarbons.

Results and Discussion

Diphenyl Sulfide/Cl Complexes. The transient spectra obtained 100 ns after pulse radiolysis are shown in Fig. 1 for 10^{-3} and 10^{-1} mol dm^{-3} DPS in 1,2-dichloroethane. The 780 nm band observed in 1,2-dichloroethane is assigned to the diphenyl sulfide radical cation, based on the previous results obtained by γ-radiolysis of DPS in halocarbon matrices at 77 K.[13] The radical cation decayed with 2nd order kinetics (Fig. 1), independent of concentration of DPS. The 340 and 520 nm bands become more intense as the DPS concentration increases (Fig. 1A). The lifetimes of these bands were identical. These results imply that these two bands are related to the same transient species. While the 780 nm band was not observed in CCl_4, the other UV-vis bands were observed in CH_2Cl_2 (340, 540, and 790 nm) and CCl_4 (340 and 505 nm) as well. These bands are assigned to the π-complexes of DPS with a chlorine atom, based on the similarity of the band position and spectral shape of various arene/Cl π-complexes.[5] Reaction rate constants of $(1—2)\times10^{10}$ $dm^3 mol^{-1} s^{-1}$ were obtained in CCl_4 and 1,2-dichloroethane, applying the half lifetimes of chlorine atoms, 140 ns[14] and 4.6 ns,[15] respectively.

$$C_6H_5SC_6H_5 + Cl\cdot \longrightarrow C_6H_5SC_6H_5/Cl\cdot \qquad (1)$$

In 1,2-dichloroethane and CH_2Cl_2, successive irradiation by a laser pulse caused photobleaching of the complex bands, as illustrated in Fig. 2. Photobleaching was induced by laser irradiation at both 355 (Φ=0.05±0.01) and 532 nm (Φ=0.06±0.01). It was completed within 10 ns, which is below the time resolution of the present experiment. The degree of the photobleaching was proportional to the laser intensity, indicating a one-photon process. On the contrary, the photobleaching was not observed for DPS/Cl complexes in CCl_4 even the DPS concentration range up to 0.3 mol dm^{-3}. Therefore, the reaction of the excited DPS/Cl complexes with solute DPS is inefficient. However, upon addition of hydrogen containing solutes (such as CH_2Cl_2, cyclohexane, and 2-methyl-2-propanol) to the CCl_4 solutions, photobleaching was observed as illustrated in Fig. 3. The quantum yields determined are listed in Table 1. The decrease of the initial optical density is due to the competitive reaction of chlorine atoms between DPS (Eq. 1) and the additives (Eq. 2).[16]

$$RH + Cl\cdot \longrightarrow R\cdot + HCl \qquad (2)$$

Diphenyl Sulfide/Br Complexes. The absorption spectrum of DPS/Br produced on irradiation of DPS in $CBrCl_3$ exhibits two peaks at 350 and 530 nm

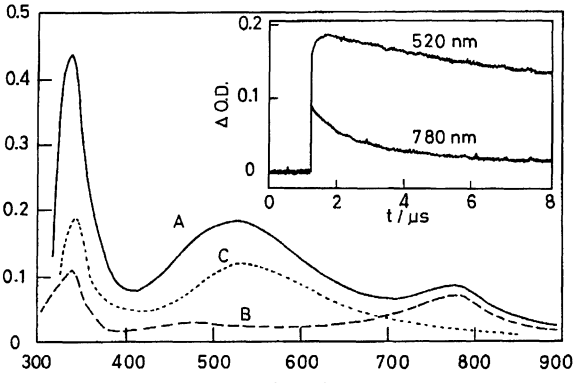

Fig. 1. Transient absorption spectra obtained 100 ns after pulse radiolysis of (A) 10^{-1} and (B) 10^{-3} mol dm^{-3} diphenyl sulfide in 1,2-dichloroethane and (C) 3×10^{-3} mol dm^{-3} diphenyl sulfide in $CBrCl_3$. Inset: decay traces for 10^{-1} mol dm^{-3} diphenyl sulfide in 1,2-dichloroethane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

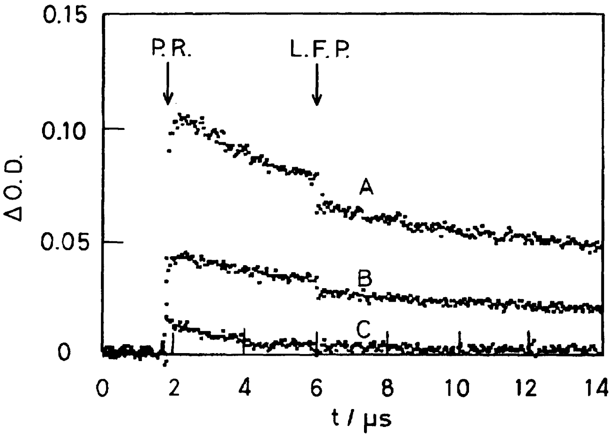

Fig. 2. Combined pulse radiolysis (P. R.) and laser flash photolysis (L. F. P.) of 0.3 mol dm^{-3} diphenyl sulfide in 1,2-dichloroethane. λ_{ex}=532 nm. λ_{obsd}: (A) 340, (B) 500, (C) 790 nm.

Table 1. Quantum Yields for Photobleaching of Diphenyl Sulfide (DPS)/Cl and DPS/Br Complexes

Complexes	Solvent	λ_{ex}/nm	Φ_{bleach}
DPS/Cl·	1,2-Dichloroethane	355	0.05±0.01
		532	0.06±0.01
	CH_2Cl_2	532	0.05±0.01
	CCl_4	532	0
	CCl_4/CH_2Cl_2 (9 : 1)	532	0.02±0.005
	CCl_4/*t*-BuOH (9 : 1)	532	0.07±0.01
	CCl_4/cyclohexane (9 : 1)	532	0.10±0.01
DPS/Br·	$CBrCl_3$	532	0
	$CBrCl_3$/cyclohexane (9 : 1)	532	0

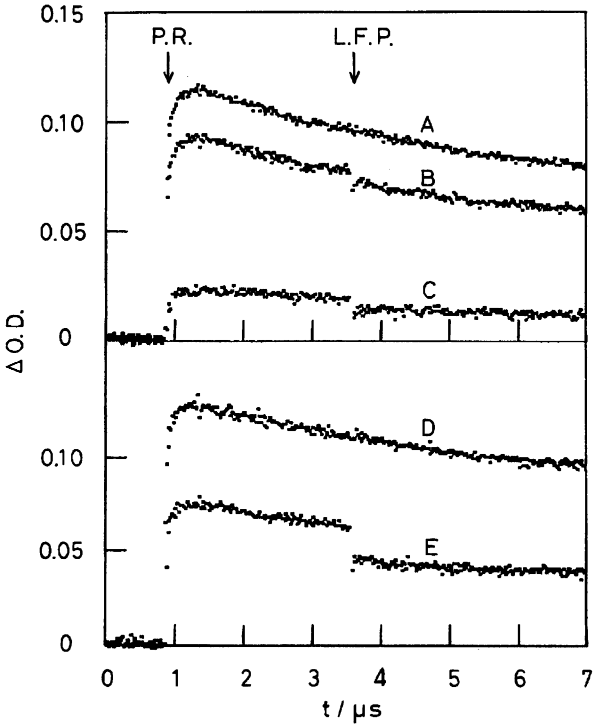

Fig. 3. Effects of additives on the reaction of the excited diphenyl sulfide (DPS)/Cl complex in CCl_4. $\lambda_{ex} = 532$ nm. $\lambda_{obsd} = 340$ nm. (A) 3×10^{-2} mol dm^{-3} DPS, (B) 3×10^{-2} mol dm^{-3} DPS, 1.6 mol dm^{-3} dichloromethane, (C) 3×10^{-2} mol dm^{-3} DPS, 1.1 mol dm^{-3} 2-methyl-2-propanol, (D) 3×10^{-1} mol dm^{-3} DPS, (E) 3×10^{-1} mol dm^{-3} DPS, 9.2×10^{-1} mol dm^{-3} cyclohexane.

as shown in Fig. 1C. Successive laser flash photolysis of the DPS/Br complexes gives no change on the kinetic traces as shown in Fig. 4. While the addition of hydrogen containing substances into CCl_4 solutions induces the photobleaching in the case of DPS/Cl complexes, DPS/Br complexes in $CBrCl_3$ were not affected by the addition of cyclohexane as shown in Fig. 4.

Mesitylene/Cl Complexes. Electron pulse irradiation of mesitylene in CCl_4 and 1,2-dichloroethane gives mesitylene/Cl π-complexes characterized by the absorption spectrum peaked at 332 and 470 nm.[5] The lifetime is longer (ca. 10 μs[6]) than most of the arene/Cl complexes. Laser induced permanent photobleaching was observed in both CCl_4 and 1,2-dichloroethane with a quantum yield of 0.10±0.01 (Table 2). Figure 5 shows laser power dependence of the photobleaching observed at 330 nm with excitation at 355 nm. The magnitude of the photobleaching was proportional to the incident laser intensity. These results indicate that the photobleaching is a one photon process. Figure 6 shows concentration effects of mesitylene in 1,2-dichloroethane on the photobleaching. Changing mesitylene concentration from 0.0018 to 0.36 mol dm^{-3} gives no effect on the quantum yield of the permanent photobleaching. These results indicate the photobleaching is indepen-

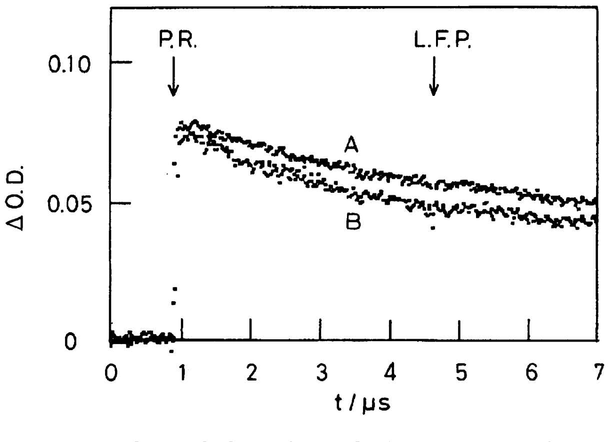

Fig. 4. Pulse radiolysis–laser flash photolysis of diphenyl sulfide in $CBrCl_3$. $\lambda_{ex} = 532$ nm. $\lambda_{obsd} = 560$ nm. (A) 3×10^{-3} mol dm^{-3} DPS, (B) 3×10^{-3} mol dm^{-3} DPS, 4.6×10^{-1} mol dm^{-3} cyclohexane.

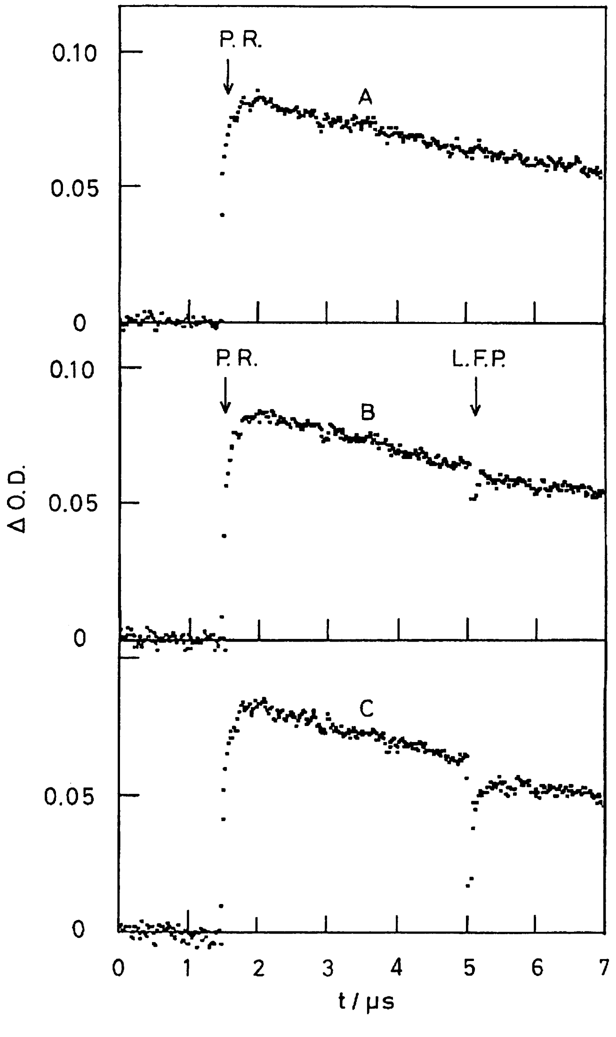

Fig. 5. Pulse radiolysis–laser flash photolysis of mesitylene (3.6×10^{-1} mol dm^{-3}) in 1,2-dichloroethane. $\lambda_{ex} = 355$ nm. $\lambda_{obsd} = 330$ nm. Incident laser intensity: (A) 0, (B) 0.95, (C) 3.2 mJ/pulse.

Table 2. Quantum Yields for Photobleaching of Mesitylene/Cl and Mesitylene/Br Complexes

Complexes	Solvent	λ_{ex}/nm	Φ_{bleach}
Mesitylene/Cl·	1,2-Dichloroethane	355	0.10±0.01
	CCl_4	355	0.10±0.01
Mesitylene/Br·	$CBrCl_3$	532	0
	$CBrCl_3$/cyclohexane (9 : 1)	532	0

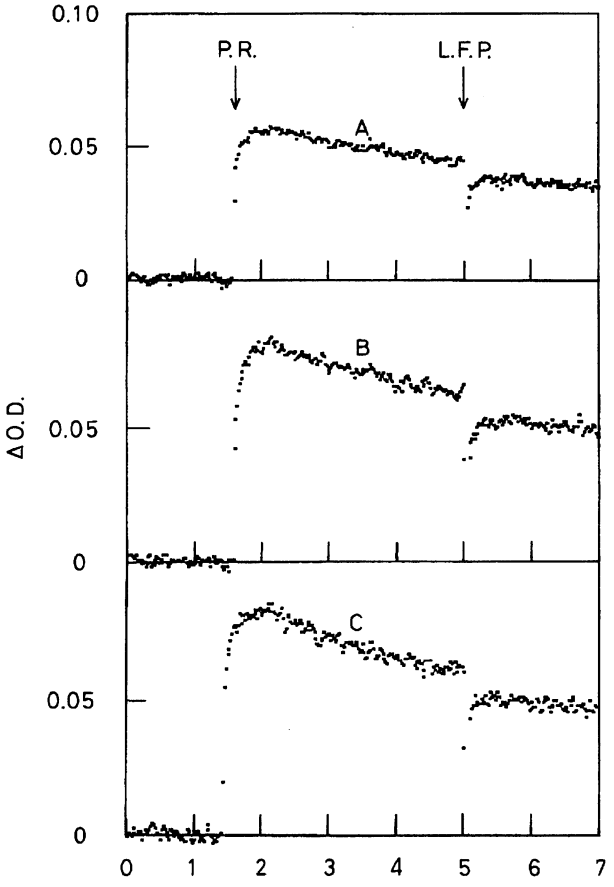

Fig. 6. Pulse radiolysis–laser flash photolysis of mesitylene in CCl_4. λ_{ex}=355 nm. λ_{obsd}=330 nm. Incident laser intensity is 4.3 mJ/pulse. Mesitylene concentration: (A) 1.8×10^{-3}, (B) 3.6×10^{-2}, (C) 3.6×10^{-1} mol dm^{-3}.

dent of solvents and of mesitylene concentration.

Mesitylene/Br Complexes. Mesitylene/Br complexes were produced on irradiation of mesitylene in $CBrCl_3$. The absorption maximum was at 525 nm as reported.[5] The mesitylene/Br complexes were excited with the 532 nm light about 800 ns after the radiolysis pulse. The transient absorption was measured at 560 nm. No photobleaching was observed as shown in Fig. 7.

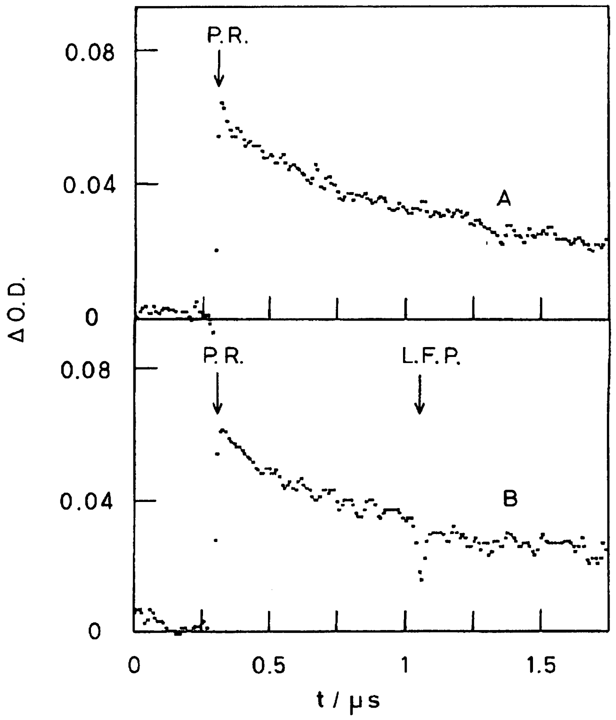

Fig. 7. Pulse radiolysis–laser flash photolysis of mesitylene (1.8×10^{-1} mol dm^{-3}) in $CBrCl_3$. λ_{ex}= 532 nm. λ_{obsd}=560 nm. Incident laser intensity: (A) 0, (B) 4.3 mJ/pulse.

Photochemistry of Diphenyl Sulfide/Halogen and Mesitylene/Halogen Complexes. The solvent dependent photobleaching observed for DPS/Cl complexes and the effects of hydrogen containing additives in CCl_4 solutions indicate that the permanent photobleaching is due to the reaction of the excited DPS/Cl complexes with the solvent, i.e., intermolecular hydrogen abstraction. On the other hand, DPS/Br complexes show no photochemistry even in the presence of cyclohexane. These observations can be summarized in the following schemes (Schemes 1 and 2);

While the intermolecular hydrogen abstraction was substantiated for the excited DPS/Cl complexes, in-

$$\text{DPS} + \text{Cl}\cdot \longrightarrow \text{DPS/Cl}\cdot \xrightleftharpoons{h\nu} (\text{DPS/Cl}\cdot)^* \xrightarrow{\text{RH}} \text{DPS} + \text{HCl}$$

Scheme 1.

$$\text{DPS} + \text{Br}\cdot \longrightarrow \text{DPS/Br}\cdot \xrightleftharpoons{h\nu} (\text{DPS/Br}\cdot)^* \cancel{\xrightarrow{\text{RH}}} \text{DPS} + \text{HBr}$$

Scheme 2.

$$\mathrm{Ph(CH_3)_3 + Cl\cdot \longrightarrow Ph(CH_3)_3/Cl\cdot \overset{h\nu}{\rightleftharpoons} (Ph(CH_3)_3/Cl\cdot)^* \longrightarrow Ph(CH_3)_2(\dot{C}H_2) + HCl}$$

Scheme 3.

$$\mathrm{Ph(CH_3)_3 + Br\cdot \longrightarrow Ph(CH_3)_3/Br\cdot \overset{h\nu}{\rightleftharpoons} (Ph(CH_3)_3/Br\cdot)^* \nrightarrow Ph(CH_3)_2(\dot{C}H_2) + HBr}$$

Scheme 4.

Table 3. Bond Dissociation Energies

Compound	E/kJ mol^{-1}	Ref.
Phenyl-H	464.0	19)
t-C_4H_9O-H	439.7	19)
H-Cl	431.62	19)
$CHCl_2$-H	420.9	19)
$C(OH)(CH_3)_2(CH_2)$-H	401	20)
Cyclohexyl-H	399.6	19)
$C_6H_5CH_2$-H	368.2	19)
H-Br	366.35	19)

tramolecular hydrogen abstraction is proposed for the excited mesitylene/Cl π-complexes based on the solvent independent photobleaching. Excitation of the mesitylene/Br complexes, however, induced no photochemistry. Therefore, the photochemistry of the mesitylene/halogen complexes can be summarized as follows (Schemes 3 and 4),

Present results demonstrate that photochemical reactions of the excited DPS/Cl and Br complexes are fast processes which complete within 10 ns. Intermolecular and intramolecular hydrogen abstraction occurs predominantly in the presence of the chlorine complexes, while deactivation occurs exclusively for the bromine complexes. The difference in reactivities of the excited states can be attributed to the reactivities of the chlorine atom and the bromine atom. Table 3 shows the bond dissociation energies of C–H, H–Cl, and H–Br. In the present experimental conditions the hydrogen abstraction by chlorine atoms is exothermic except for phenyl-H. On the other hand, the hydrogen abstraction by bromine atoms is endothermic. Consequently, intermolecular hydrogen abstraction is the main photochemical process for the DPS/Cl complexes. Since the C–H bond dissociation energy of methyl groups of substituted benzene is the smallest among the C–H bonds of the substances used, the solvent independent intramolecular hydrogen abstraction occurs predominantly in the case of the mesitylene/Cl complexes.

The authors are very grateful to Dr. Sadashi Sawamura and Messrs. Hiroaki Tanida and Koichi Sato for their help in operating the linac.

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15) The half lifetime of chlorine atoms in 1,2-dichloroethane was determined from the buildup of DMSO/Cl complexes ($\lambda_{max}=400$ nm) and $k(Cl\cdot + DMSO) = 7\times10^9$ dm^3 mol^{-1} s^{-1}.[7)]

16) The rate constants are $k_2(CH_2Cl_2+Cl\cdot)=3.7\times10^7$,[7)] k_2(cyclohexane + Cl·) = 6×10^9,[17)] and k_2(2-methyl-2-propanol+Cl·)$=3.2\times10^9$ mol^{-1} dm^3 s^{-1}.[18)]

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