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The Dechlorination of Polychlorinated Biphenyls by UV-irradiation. VIII. Reactions of 2,3- and 3,4-Dichlorobiphenyl in a 2-Propanol Solution

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The photodechlorinations of 2,3-dichlorobiphenyl (2,3-DCB) and 3,4-dichlorobiphenyl (3,4-DCB) in 2-propanol gave 3-chlorobiphenyl and 4-chlorobiphenyl respectively. The quantum yields of monochlorobiphenyl formation were 0.2 for 2,3-DCB and 0.06 for 3,4-DCB, independent of the substrate concentration and the wavelength of the exciting light. On the basis of the results obtained in quenching experiments using *cis*-1,3-pentadiene, it was concluded that 2,3-DCB was photodechlorinated exclusively in the excited singlet state, while 3,4-DCB was photodechlorinated in both excited singlet and triplet states. In the case of 3,4-DCB, the relative contributions of excited singlet and triplet states to the total dechlorination were evaluated as 0.8 and 0.2 respectively. The participation of the excited triplet state in the photodechlorination of 3,4-DCB was ascertained both by quenching reactions with biacetyl as a quencher and by photosensitized dechlorinations with acetone and acetophenone as sensitizers.

In connection with the environmental breakdown of pollutants initiated by sunlight, the photodechlorination of polychlorobiphenyls has attracted the interests of several authors.¹⁾ Safe and Hutzinger²⁾ found that 2,2′,4,4′,6,6′-hexachlorobiphenyl was photochemically decomposed by the irradiation of 310 nm. Schuetz *et al.*³⁾ proposed that the excited triplet state was involved in the photodechlorination of six symmetrical tetrachlorobiphenyls, based on the effective quenching for the reaction by 1,3-cyclohexadiene.

Recently Bunce *et al.*⁴,⁵⁾ reported that the excited triplet state plays an important role in the photodechlorination of chlorobiphenyls; he based this conclusion on the following grounds: (1) The xenon assistance of the reaction, and (2) the quenching of the reaction by biacetyl. However, the reactivity of the photodechlorination of polychlorobiphenyls depends on the position of the eliminated chlorine atom and is largely affected by the presence of ortho chlorine atoms.³,⁴,⁶⁾ The same positional dependence of reactivity has also been found in the photodechlorination of polychlorinated benzenes, and it has been clarified that the reaction involves not only an excited triplet state, but also an excited singlet state.⁷⁾

In this paper, the photodechlorinations of 2,3-dichlorobiphenyl (2,3-DCB) and 3,4-dichlorobiphenyl (3,4-DCB) were studied by photoquenching and photosensitization examinations. Also, the reactivities and the multiplicities of the excited state responsible for the reactions were discussed. A reaction mechanism will also be proposed.

Experimental

Materials. The 2,3-DCB and 3,4-DCB were prepared and purified as reported in a previous paper.⁶⁾ The *cis*-1,3-pentadiene, biacetyl, acetophenone, and triethylamine were used after distillation. The 2-propanol (Dotite Luminasol for fluorometry; Wako Pure Chemical Co., Ltd., Osaka) and acetone (solvent for pesticide residue analysis; Wako Pure Chemical Co., Ltd., Osaka) were used without further purification.

Apparatus. Irradiation was carried out on a Hitachi MPF-4 spectrofluorometer equipped with a 150-W Xenon lamp and a grating monochrometer (Czerny-Turner mounting). Using the maximum slit width, a monochromatic light was obtained with a wavelength purity of 20 nm; its intensity was about 2×10^{15} photons s^{-1} at 300 nm.

The amount of monochlorobiphenyls produced in the irradiated reaction mixture was determined with a JEOL Model D-100 gas chromatograph-mass spectrometer system which was equipped with a 2 m×3 mmϕ stainless steel column packed with 10% SE-30 on 80—100 mesh chromosorb A (HMDS). The magnetic field of the mass spectrometer was fixed at m/e 188 to detect the molecular-ion peak of monochlorobiphenyls.

GLC analysis was conducted on a JEOL 20-K gas chromatograph with a flame-ionization detector. A glass capillary column, 60 m×1 mmϕ, with PEG-20M (Chromato Research Co.) was used to separate the 3-chlorobiphenyl from the 4-chlorobiphenyl.

The number of photons absorbed by the reaction mixture was determined by the use of a chemical actinometer of potassium tris(oxalato)ferrate(III). A Union Giken SM-401 spectrophotometer and a Hitachi MPF-4 spectrofluorometer were used for the measurement of the UV absorption spectra and the emission spectra respectively.

Procedures. After the 2-propanol solution (4.5 cm^3) in a quartz reaction cell had been bubbled with purified nitrogen for 5 min, the cell was sealed and irradiated. Irradiation was continued until the concentration of monochlorobiphenyls increased to about 10 μmol dm^{-3} in the irradiated reaction mixture.

Quenching studies were carried out at the excitation of 290 nm to avoid the direct excitation of *cis*-1,3-pentadiene. The incident light was absorbed only by dichlorobiphenyl molecules. The concentrations of 2,3-DCB and 3,4-DCB were 20 mmol dm^{-3} and 1.5 mmol dm^{-3} respectively.

In photosensitizing experiments, the wavelength of the exciting light was selected so that the incident light was absorbed only by sensitizer molecules. The concentrations of the sensitizers were adjusted so that about 90% of the incident light was absorbed. The wavelengths and concentrations employed were as follows: 320 nm and 2.0 mol dm^{-3} for acetone; 340 nm and 40 mmol dm^{-3} for acetophenone, and 366 nm and 20 mmol dm^{-3} for benzophenone. The concentrations of 2,3-DCB and 3,4-DCB were both 1.5 mmol dm^{-3}.

Results and Discussion

The Quantum Yield for Dechlorination. 2,3-DCB and 3,4-DCB gave 3-chlorobiphenyl and 4-chlorobiphenyl respectively upon UV irradiation in 2-propanol, as was reported in our previous paper.[6] A further, detailed examination of the products revealed that the direct irradiation of 3,4-DCB afforded 4-chlorobiphenyl in a 92% yield and 3-chlorobiphenyl in an 8% yield. The quantum yields of monochlorobiphenyl formation are listed in Table 1. These values are comparable to the quantum yields of dechlorination in cyclohexane for six tetrachlorobiphenyls reported by Schuetz *et al.*[3] The chlorine atom at the ortho position of 2,3-DCB was found to have a much higher elimination efficiency than the chlorine atom at the meta position of 3,4-DCB.

Bunce *et al.*[8] reported that the quantum yield of 1-chloronaphthalene rose with an increase in the substrate concentration. Excimer formation was considered to stimulate the photoreduction of 1-chloronaphthalene to naphthalene. On the contrary, the quantum yield of monochlorobenzene photolysis in cyclohexane has been reported to decrease with an increase in the concentration of chlorobenzene.[9] Mori *et al.*[10] found that the photolysis of chlorobenzene in the gas phase depended on the excitation wavelength. Our examinations, however, showed that no essential change was observed in the reactivities of 2,3-DCB and 3,4-DCB upon changes in the wavelength of irradiation and the substrate concentration (Table 1). Excimer formation is, therefore, not considered to play an important role in the photodechlorination of 2,3-DCB and 3,4-DCB.

The Quenching Experiment Using cis-*1,3-Pentadiene.* As Fig. 1 shows, a good linear Stern-Volmer plot was obtained for 2,3-DCB with a slope of 3.1 dm^3 mol^{-1} and an intercept equal to unity. On the other hand, the Stern-Volmer plot for 3,4-DCB gave a straight line with an intercept different from unity, indicating that two different excited states are involved in the photoreaction. The fluorescences of these dichlorobiphenyls were quenched to an extent similar to their photodechlorinations by *cis*-1,3-pentadiene.[11]

Table 1. Wavelength effect and concentration effect on dechlorination quantum yield in 2-propanol solution

Wavelength nm	Concn mol dm^{-3}	Φ_r [a)] 2,3-DCB	 3,4-DCB
250	1.5×10^{-2}	0.21	0.063
	1.5×10^{-3}	0.18	0.053
	1.5×10^{-4}	0.22	0.056
290	1.5×10^{-2}	0.18	0.056
	1.5×10^{-3}		0.064
	1.5×10^{-4}		0.064
300	1.5×10^{-2}	0.15	
310	1.5×10^{-2}		0.059

a) Φ_r is the quantum yield of monochlorobiphenyl formation.

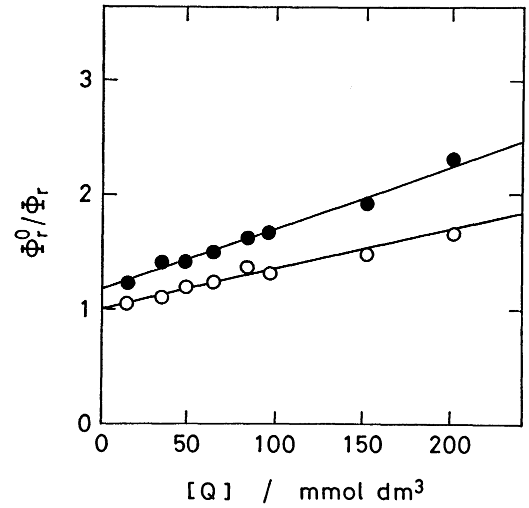

Fig. 1. Stern-Volmer plots for the quenching of dechlorination in 2-propanol solution by *cis*-1,3-pentadiene. ○: 2,3-DCB (20 mmol dm^{-3}), ●: 3,4-DCB (1.5 mmol dm^{-3}).

These results suggest that the dechlorination of 2,3-DCB occurs virtually all from the excited singlet state, while that of 3,4-DCB occurs from both excited singlet and triplet states.

Since the quantum yield for the dechlorination of 2,3-DCB from the excited singlet state is 0.2, its quantum yield for intersystem crossing must be smaller than that of biphenyl, 0.81,[12] in spite of the internal heavy-atom effect of chlorine atoms. Taking into consideration the fact that biphenyl has a planar structure in its excited singlet state, whereas it is twisted in the ground state in solution,[13] the chlorine atom at the 2-position in 2,3-DCB must be very labile in its excited state because of the large steric hindrance. This elimination is presumed to reduce the intersystem crossing efficiency of 2,3-DCB.

In the case of 3,4-DCB, the Stern-Volmer expression can be written by Eq. 1:

$$\frac{\Phi_r^o}{\Phi_r}=\frac{(1+k_q^S\tau_s[Q])(1+k_q^T\tau_T[Q])}{1+\{\Phi_r^S/(\Phi_r^S+\Phi_r^T)\}k_q^T\tau_T[Q]}, \tag{1}$$

where Φ_r^o and Φ_r designate the quantum yields for the dechlorination of 3,4-DCB measured in the absence and in the presence of a quencher respectively, Φ_r^S and Φ_r^T the quantum yields for the dechlorination of 3,4-DCB from excited singlet and triplet states respectively in the absence of a quencher ($\Phi_r^o=\Phi_r^S+\Phi_r^T$), k_q^S and k_q^T the rate constants for quenching excited singlet and triplet states of 3,4-DCB respectively, τ_S and τ_T the lifetimes of excited singlet and triplet states of 3,4-DCB respectively, and [Q] is the concentration of the quencher, Q.

At sufficiently high concentrations of Q, Eq. 1 can be rewritten as Eq. 2:

$$\frac{\Phi_r^o}{\Phi_r}\simeq\left(\frac{\Phi_r^S+\Phi_r^T}{\Phi_r^S}\right)k_q^S\tau_S[Q]+\left(\frac{\Phi_r^S+\Phi_r^T}{\Phi_r^S}\right)\left(1-\frac{\Phi_r^Tk_q^S\tau_S}{\Phi_r^Sk_q^T\tau_T}\right). \tag{2}$$

Since τ_T is generally much larger than τ_S, the term of $\Phi_r^Tk_q^S\tau_S/(\Phi_r^Sk_q^T\tau_T)$ can be neglected. Thus, Eq. 2 can be approximated by Eq. 3:

$$\frac{\Phi_r^o}{\Phi_r} \approx \left(\frac{\Phi_r^S + \Phi_r^T}{\Phi_r^S}\right) k_q^S \tau_S[Q] + \frac{\Phi_r^S + \Phi_r^T}{\Phi_r^S} . \tag{3}$$

A plot of Φ_r^o/Φ_r *versus* [Q] should give a straight line, with an intercept of $(\Phi_r^S + \Phi_r^T)/\Phi_r^S$ and a slope of $(\Phi_r^S + \Phi_r^T) k_q^S \tau_S / \Phi_r^S$.

From the intercept of 1.2 for the straight line of 3,4-DCB (Fig. 1), the contribution of each excited state to the total dechlorination was evaluated to be 0.8 for the excited singlet state and 0.2 for the excited triplet state. From the slope and intercept, the Stern-Volmer constant of 3,4-DCB, $k_q^S \tau_S$, was calculated to be 4.4 $dm^3\,mol^{-1}$, while the value of 3.1 $dm^3\,mol^{-1}$ was obtained for 2,3-DCB.

The Quenching of 3,4-DCB Photodechlorination by Biacetyl. When [Q] is low enough to make $k_q^S \tau_S [Q] \ll 1$,[14] Eq. 1 can be approximated as Eq. 4:

$$\frac{\Phi_r^o}{\Phi_r} \approx \frac{1 + k_q^T \tau_T [Q]}{1 + \{\Phi_r^S/(\Phi_r^S + \Phi_r^T)\} k_q^T \tau_T [Q]} . \tag{4}$$

Equation 4 can be rewritten as Eq. 5:

$$\frac{1}{\Phi_r^o/\Phi_r - 1} \approx \frac{1 + \Phi_r^S/\Phi_r^T}{k_q^T \tau_T [Q]} + \frac{\Phi_r^S}{\Phi_r^T} . \tag{5}$$

A linear plot of the $(\Phi_r^o/\Phi_r - 1)$ reciprocal versus the [Q] reciprocal is predicted by Eq. 5, with an intercept of Φ_r^S/Φ_r^T and a slope of $(1 + \Phi_r^S/\Phi_r^T)/(k_q^T \tau_T)$. Figure 2 depicts the linear plot in the case of 3,4-DCB. In this experiment, biacetyl was used as a quencher in place of *cis*-1,3-pentadiene in the concentration range of 0.3—2.0 mmol dm^{-3}. The least-squares fits of the plots gave the slope of 1.6×10^{-3} $dm^3\,mol^{-1}$ and the intercept of 2.2. From the value of the intercept, the contribution of each excited state to the total dechlorination was evaluated to be 0.7 for the excited singlet state and 0.3 for the excited triplet state.[15] It should be noted that the excited singlet state plays an important role in the photodechlorination of dichlorobiphenyls, while in the case of other chlorobiphenyls[3-5] the photodechlorination takes place through their excited triplet states.

The double reciprocal linear plots were not affected by the change in the concentrations of 3,4-DCB.[16] Consequently, the dechlorination of 3,4-DCB from its excited triplet state is considered to be concentration-independent, like the dechlorination from its excited singlet state.

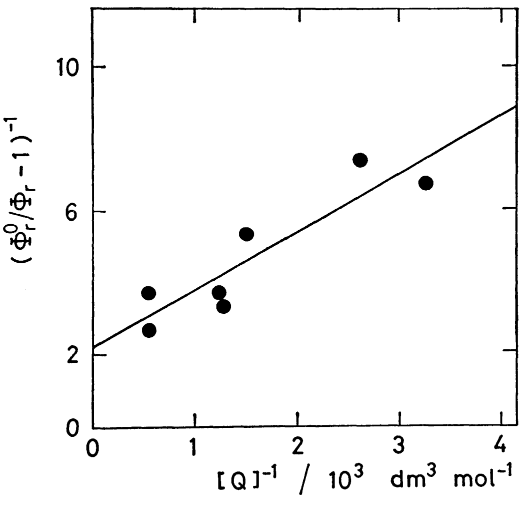

Fig. 2. Modified Stern-Volmer plot for the quenching of 3,4-DCB dechlorination in 2-propanol solution by biacetyl. 3,4-DCB: 1.5 mmol dm^{-3}.

The results of quenching experiments at high concentrations of *cis*-1,3-pentadiene and at low concentrations of biacetyl are summarized in Table 2. A fairly good agreement is observed between them.

Photosensitized Dechlorination. Table 3 summarizes the results of dechlorination photosensitized by several ketones. Since the dechlorination of 2,3-DCB was sensitized by neither acetone nor acetophenone, the excited triplet state of 2,3-DCB was considered to be unreactive toward dechlorination. The dechlorination of 3,4-DCB was not sensitized by benzophenone, while acetone and acetophenone both sensitized the photoreaction of 3,4-DCB to give 3-chlorobiphenyl as the sole product. These photosensitization experiments revealed that the dechlorination of 3,4-DCB takes place from the excited triplet state as well as the excited singlet state, while the dechlorination of 2,3-DCB proceeds exclusively from the excited singlet state. As is shown in Table 3, sensitization by acetophenone was much less efficient than that by acetone. Benzophenone failed to sensitize the dechlorination of 3,4-DCB. The triplet energies of these ketones are as follows;[12] benzophenone, $E_T = 289$ kJ mol^{-1}; acetophenone, $E_T = 310$ kJ mol^{-1}; acetone, $E_T = 330$ kJ mol^{-1}. The triplet energy of 3,4-DCB was estimated to be 268 kJ mol^{-1} from its phosphorescence spectrum in a EPA glass at 77 K. Although benzophenone has a higher triplet energy than 3,4-DCB by 21 kJ mol^{-1}, the photosensitized dechlorination of 3,4-DCB by benzophenone was not observed.

Wagner[17] pointed out that the quenching efficiencies of biphenyl for the photoreduction of benzophenone by benzhydrol was unexpectedly inefficient. He explained this finding on the basis of a difference in the

Table 2. CONTRIBUTION OF SINGLET AND TRIPLET STATES TO PHOTODECHLORINATION IN 3,4-DCB

Quencher	Relative quantum yield of photodechlorination from	
	Singlet	Triplet
cis-1,3-Pentadiene	0.8	0.2
Biacetyl	0.7	0.3

Table 3. PHOTOSENSITIZED DECHLORINATION BY KETONES

Compound	Sensitizer	$\frac{E_T{}^{a)}}{\text{kJ mol}^{-1}}$	$\Phi_{app}{}^{b)}$	Excitation wavelength/nm
2,3-DCB	Acetone	330	0	320
	Benzophenone	289	0	366
3,4-DCB	Acetone	330	0.0097	320
	Acetophenone	310	0.0003	340
	Benzophenone	289	0	366

a) E_T is the triplet energy of a sensitizer. b) Φ_{app} is the apparent quantum yield for dechlorination and is given by:

$$\Phi_{app} = \frac{\text{number of monochlorobiphenyl molecules formed}}{\text{number of quanta absorbed by a sensitizer}} .$$

Table 4. Acetone-sensitized photodechlorination of 3,4-DCB in the presence of TEA

[TEA] / mol dm^{-3}	Φ_{app} a)	N_{rel} b)	$\Phi_{\mathrm{app}}/N_{\mathrm{rel}}$
0	0.0097	1.00	0.0097
2×10^{-3}	0.0046	0.93	0.0049
2×10^{-2}	0.0015	0.58	0.0026
2×10^{-1}	0.0007	0.12	0.0058

a) See Table 3. b) N_{rel} is the calculated relative number of excited triplet-state 3,4-DCB molecules formed by energy transfer from excited triplet-state acetone.

geometry of biphenyl between the ground state and the excited triplet state. The most stable conformation of ground-state biphenyl is a twisted one in solution. The dihedral angle between the two phenyl rings is 20—25°. On the other hand, excited triplet-state biphenyl is considered to take a planar conformation. Thus, the energy required to activate twisted ground-state biphenyl into its twisted excited triplet state is greater than the energy liberated by the transition from the planar excited triplet state to the planar ground state. The latter energy is estimated from the phosphorescence spectrum. This is why the intermolecular energy transfer did not take place from excited triplet-state benzophenone to ground-state 3,4-DCB, since the situation described above is also the case for 3,4-DCB.

Ohashi *et al.*[18] reported that the photodechlorination of 4-chlorobiphenyl was greatly enhanced in the presence of triethylamine (TEA) by the formation of an excited charge-transfer complex between excited singlet-state 4-chlorobiphenyl and ground-state TEA. As is shown in Table 4, the apparent quantum yield of the acetone-sensitized dechlorination of 3,4-DCB decreased with an increase in the concentration of TEA.

The following deactivating processes of excited triplet-state acetone can be assumed: (1) Unimolecular decay ($k_q^T \approx 2\times10^5$ s^{-1}),[19a] (2) hydrogen abstraction from 2-propanol (k_H[2-propanol] $\approx 1\times10^7$ s^{-1}),[19b] (3) energy transfer to 3,4-DCB (k_{en}[3,4-DCB] $\approx 7\times10^6$ s^{-1}),[19c] and (4) electron transfer to TEA ($k_{el} \approx 3\times10^8$ dm^3 mol^{-1} s^{-1}).[19b] The relative number, N_{rel}, of excited triplet-state 3,4-DCB molecules formed by energy transfer from excited triplet-state acetone was calculated as a function of the concentration of TEA by assuming the above processes from (1) to (4) (Table 4). By comparing these values with the apparent quantum yields for dechlorination one can see that the efficiency of photosensitized dechlorination, $\Phi_{\mathrm{app}}/N_{\mathrm{rel}}$, does not increase in the presence of TEA. Furthermore, as has been described in the previous section, the dechlorination of 3,4-DCB from its excited triplet state does not depend on its concentration. Accordingly, electron-transfer processes, such as exciplex and excimer formations, seem unlikely in the dechlorination of triplet-state 3,4-DCB. It may thus be concluded that the homolytic fission of the carbon-chlorine bond takes place in excited triplet-state 3,4-DCB.

From the quantum yield for the dechlorination and the contribution of the excited triplet state to the total dechlorination, the quantum yield for the dechlorination of 3,4-DCB from excited triplet state is evaluated to be 0.02. Since the carbon-chlorine bond-dissociation energies for aromatic chloro compounds are about 356 kJ mol^{-1},[20] the triplet-sensitized photodechlorination of 3,4-DCB by acetone or acetophenone would be endothermic.

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15) The Stern-Volmer constant for quenching the excited triplet state of 3,4-DCB by biacetyl, $k_q^T\tau_T$, is evaluated to be 1.94×10^3 dm^3 mol^{-1}.

16) At different concentrations of 3,4-DCB, the slope and intercept for the line expressed by Eq. 5 were obtained as follows: 0.7×10^{-3} mol dm^{-3} and 2.4 at 0.15 mmol dm^{-3} of 3,4-DCB; 1.0×10^{-3} mol dm^{-3} and 2.0 at 0.9 mmol dm^{-3}; 1.6×10^{-3} mol dm^{-3} and 2.2 at 1.5 mmol dm^{-3}; 1.3×10^{-3} mol dm^{-3} and 3.3 at 2.5 mmol dm^{-3}.

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