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The Dechlorination of Polychlorinated Biphenyls by UV-irradiation. IX. Reactions of Monochlorobiphenyls in a 2-Propanol Solution

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The multiplicity of the photo-excited state responsible for the dechlorination reaction of monochlorobiphenyls was determined in 2-propanol. Linear Stern-Volmer plots were obtained by the use of 1,3-cyclohexadiene for the dechlorination reactions of 2- and 3-chlorobiphenyl; the slopes were 35.7 and 11.0 $dm^3\ mol^{-1}$ respectively. Fluorescence emissions were also quenched, and the quenching constants for 2- and 3-chlorobiphenyls were in accord with the respective values of the slope obtained from the Stern-Volmer plot for the reaction. The reaction of 4-chlorobiphenyl was quenched by *cis*-1,3-pentadiene, but was accelerated by 1,3-cyclohexadiene. Photosensitized dechlorinations of monochlorobiphenyls took place with several ketones, such as acetone and acetophenone. These sensitized reactions were, however, very inefficient compared with the reactions in the direct excitations, except in the case of 4-chlorobiphenyl. It was, then, concluded that the dechlorinations of 2- and 3-chlorobiphenyl occurred only from the excited singlet state, while that of 4-chlorobiphenyl took place predominantly from the excited triplet state.

In the preceding paper[1] the authors proposed that the excited singlet state plays an important role in the photodechlorinations of 2,3- and 3,4-dichlorobiphenyls, and that the dechlorinations do not proceed through excimer formation between the excited-state and ground-state chlorobiphenyls, but through simple homolytic fission in their excited states. Contrary to our results, several authors[2,3] have confirmed that the photodechlorinations of chlorobiphenyls take place through the excited triplet state. These results were obtained mainly with respect to highly chlorinated biphenyls, in which the intersystem crossings are enhanced by the internal heavy-atom effect, so that the reaction from the excited triplet state will tend to be emphasized.

In the present paper, the quenching and sensitized studies were applied to the dechlorination of 2-chlorobiphenyl (2-CB), 3-chlorobiphenyl (3-CB), and 4-chlorobiphenyl (4-CB) to make clear the excited state responsible for the reactions of the monochlorinated biphenyls. The reaction mechanism will also be discussed.

Experimental

Materials. The 2-propanol (Dotite Luminasol for fluorometry; Wako Pure Chemical) and acetone (solvent for pesticide residue analysis; Wako Pure Chemical) were used without further purification. The *cis*-1,3-pentadiene and 1,3-cyclohexadiene (Tokyo Kasei; guaranteed grade), and acetophenone (Wako Pure Chemical; guaranteed grade) were used after an ordinary distillation. The benzophenone (Wako Pure Chemical, special grade) was purified by recrystallization from ethanol. The 2-CB, 3-CB, and 4-CB were prepared by a modification of Cadogan's method.[4] The crude CBs were chromatographed several times over a silica-gel column, using hexane as the eluent, and recrystallized from ethanol. The purified CBs were contaminated by a trace of biphenyl; the contents in 2-, 3-, and 4-CB were estimated to be 0.16, 0.15, and 0.0002% respectively.

Irradiation. A solution of CBs, and the quenchers or sensitizers if necessary, was pipetted into a quartz reaction cell (4.5 ml), deaerated by bubbling nitrogen for 5 min, and then sealed. Photolyses were carried out under the following conditions: A) The reaction cell was placed in a water bath kept at 30 °C and then irradiated through an interference filter (Nihon Shinku S50ϕ, 298 nm) with a 250W highpressure mercury lamp (Ushio USH-250). B) The photolyses with a monochromatic light of an adequate purity were carried out with a Hitachi MPF-4 spectrofluorometer equipped with a 150W xenon lamp and a grating monochrometer. The intensity of incident light for reaction cell was about $(1.8—3.4)\times 10^{15}$ photons s^{-1} in the wavelength region of 290—370 nm. Actinometry was done by the method of Hatchard and Parker[5] using potassium tris(oxalate)ferrate(III).

Analysis of the Photolyzed Product. The photolyzed samples were analyzed for the formation of biphenyl as follows. GLC analysis was conducted on a JEOL 20-K gas chromatograph with a flame-ionization detector employing a 2 m×3 mmϕ stainless steel column packed with 10% SE-30 on 80—100 mesh Chromosorb A (HMDS). A JEOL Model D-100 mass spectrometer was used to estimate the trace amounts of biphenyl quantitatively; the strength of the magnetic field was fixed at m/e 154.

Absorption and Emission Spectra. The absorption spectra of sample solutions were taken on a Union Giken SM-401 spectrophotometer before and after irradiation. The fluorescences of CBs at the ambient temperature and the phosphorescence emissions at 77 K in a EPA glass were examined with a Hitachi MPF-4 spectrofluorometer.

Results and Discussion

Quenching Experiments by Dienes. The photodechlorination reactions of 2-CB and 3-CB were quenched by 1,3-cyclohexadiene in 2-propanol. As is shown in Fig. 1, both Stern-Volmer plots were linear with an intercept equal to unity; the slopes were 35.7 $dm^3\ mol^{-1}$ and 11.0 $dm^3\ mol^{-1}$ for 2-CB and 3-CB respectively. Thus, a single excited state was considered to play an important role in the dechlorinations of both 2-CB and 3-CB. The fluorescences of these chlorobiphenyls were observed in the wavelength region of 300—380 nm. In the presence of 1,3-cyclohexadiene the fluorescences were quenched with the quenching constants of 33.5 $dm^3\ mol^{-1}$ and 11.5 $dm^3\ mol^{-1}$ for 2-, and 3-CB respectively. The respective quench-

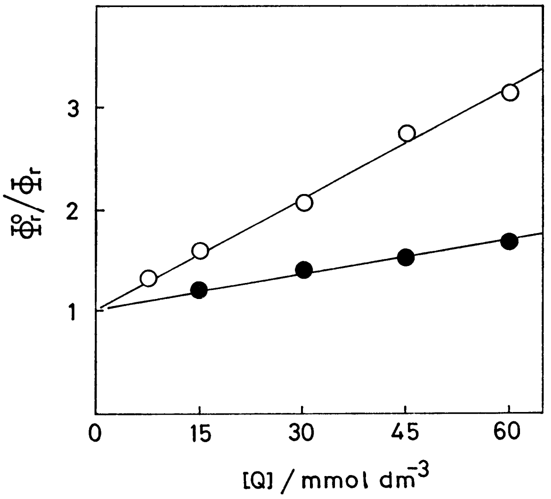

Fig. 1. Stern-Volmer plots for the quenching of dechlorination reaction by 1,3-cyclohexadiene.
○: 2-CB (15 mmol dm^{-3}), ●: 3-CB (15 mmol dm^{-3}).

ing constant of the dechlorination reactions for 2-, and 3-CB exhibits a good agreement with that of the fluorescence. Assuming a diffusion-control rate for the quenching,[6)] the lifetimes were roughly estimated to be 7 and 3 ns for 2- and 3-CB respectively from the Stern-Volmer constants in the dechlorination reactions. The value of 3—7 ns would be reasonable for the lifetime of the excited singlet-state monochlorobiphenyls; this may be compared with that of 4-CB, reported to be 1.2—1.3 ns.[7)] The dechlorination reactions of 2-, and 3-CB were concluded to take place through their excited singlet states.

The quenching reaction of 4-CB was more complicated than those of 2-, and 3-CB. A curved Stern-Volmer plot was obtained by using *cis*-1,3-pentadiene, as is shown in Fig. 2. This suggests that both excited singlet and triplet states of 4-CB are responsible for the dechlorination reaction. The slope of the curved Stern-Volmer plot decreased with the increase in the diene concentration, and the plot tend to be asymptotic to a straight line in the high-concentration ranges of diene.

As has been discussed in the preceding paper,[1)] at a sufficiently high concentration of diene, the curved Stern-Volmer plot may be approximated in the following form:

$$\frac{\Phi_r^\circ}{\Phi_r} \approx \left(\frac{\Phi_r^S+\Phi_r^T}{\Phi_r^S}\right)\kappa_q^S\tau_S[Q] + \frac{\Phi_r^S+\Phi_r^T}{\Phi_r^S} \qquad (1)$$

where Φ_r° and Φ_r are the quantum yields for the dechlorination of 4-CB measured in the absence and in the presence of a quencher respectively. Φ_r^S and Φ_r^T are the quantum yields for the dechlorination of 4-CB in the excited singlet state and the excited triplet state respectively in the absence of a quencher (namely, $\Phi_r^\circ=\Phi_r^S+\Phi_r^T$). $k_q^S\tau_S$ is the quenching constant of excited singlet-state 4-CB. [Q] denotes the concentration of the quencher, Q.

The ratio of the quantum yields for the dechlorination from the excited singlet and triplet states, Φ_r^T/Φ_r^S, can be determined from the value of the intercept. As may be seen in Fig. 2, the curved plot is not completely asymptotic to a straight line, even in high-concentration ranges of diene, but the intercept can be roughly estimated to be larger than 9. This implies that the contribution of the excited triplet state to the dechlorination of 4-CB is more than 90%. Thus, it was concluded that the dechlorination of 4-CB occurred from both excited singlet and triplet states, but predominantly from the latter state.

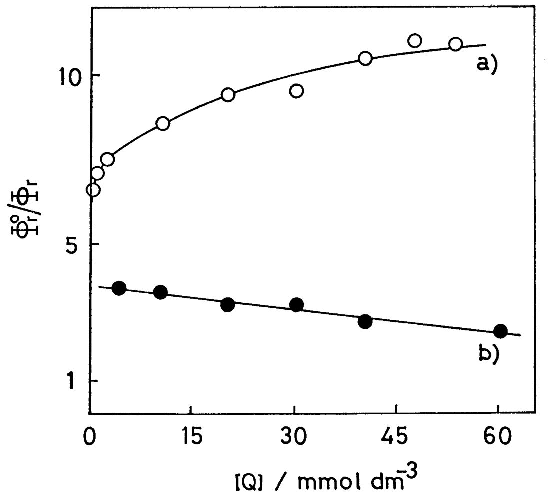

Fig. 2. Stern-Volmer plots for the quenching of dechlorination reaction of 4-CB by dienes.
○: *cis*-1,3-Pentadiene, ●: 1,3-cyclohexadiene. Concentration of 4-CB: 5—15 mmol dm^{-3}.
a) Photolyzed at 290 nm with monochrometer (Hitachi MPF-4), b) photolyzed at 298 nm through filter with 250 W high pressure mercury lamp.

Interestingly, the dechlorination of 4-CB was clearly accelerated by adding 1,3-cyclohexadiene, as is shown in Fig. 2. A similar acceleration has been found in the photo-dechlorination reaction of 4-CB with triethylamine;[8)] it was interpreted in terms of the formation of a charge-transfer complex between the excited singlet-state 4-CB and triethylamine in the ground state.

It is well known that aromatic hydrocarbons such as methylnaphthalenes in the excited singlet state interact with the ground-state dienes, and that the degree of exciplex formation increases with the decrease in the adiabatic ionization potential (I_p) of diene.[9)] The I_p values of 1,3-cyclohexadiene and *cis*-1,3-pentadiene are believed to be 7.88 and 8.42 eV[10)] respectively. This implies that 1,3-cyclohexadiene is more reactive than *cis*-1,3-pentadiene in the exciplex formation with 4-CB in the excited singlet state. Thus, 1,3-cyclohexadiene would accelerate the dechlorination of 4-CB *via* exciplex formation. On the other hand, because of the large I_p value, *cis*-1,3-pentadiene is less reactive for the exciplex formation and the charge separation in the exciplex ($CB^{\delta-}\cdots Q^{\delta+}$) would be small, so that dechlorination would not take place in this case.

Photosensitized Dechlorination. Table 1 summarizes the results of sensitizations. It must be noted that the yield shown in Table 1 does not represent the quantum yield for a dechlorination reaction from the excited triplet-state CB, since the efficiency of

TABLE 1. APPARENT QUANTUM YIELDS SENSITIZED WITH KETONES[a–d]

Compound	Acetone	Acetophenone	Benzophenone
2-CB	0.0024		0.00010
3-CB	0.00015		
4-CB	0.0041	0.00015	0.00010

a) Apparent quantum yield $= \dfrac{\text{formation of biphenyl}}{\text{photons absorbed by ketone}}$. b) The excitations of these ketones were carried out at 320, 320, and 366 nm for acetone, acetophenone, and benzophenone respectively. c) The concentrations of sensitizers were as follows: acetone, 2 mol dm^{-3}; acetophenone, 2×10^{-2} mol dm^{-3}; benzophenone, 2×10^{-2} mol dm^{-3}. d) Measurements were done in duplicate, and the results were averaged.

energy transfer from the excited triplet ketone to the ground-state CB is not evaluated. The efficiency, (Φ_{et}) can be represented by a familiar equation:

$$\Phi_{et} = \frac{k_{et}[\mathrm{CB}]}{k_d + k_h[i\text{-PrOH}] + k_{et}[\mathrm{CB}]}\Phi_{ic}, \qquad (2)$$

where k_{et} is the rate constant of energy transfer from triplet ketone to ground-state CB, k_d is the rate constant of hydrogen abstraction from 2-propanol in triplet ketone, and Φ_{ic} is the quantum yield of the intersystem crossing of ketone.

By the use of the values of the rate constants found in the literature, the efficiency could be tentatively estimated. The k_d, k_h, and Φ_{ic} values of acetone have been reported to be 2.0×10^5 s^{-1}, 1×10^6 dm^3 mol^{-1} s^{-1}, and 1.0[11] respectively. Thus, the efficiency of energy transfer from triplet acetone to CB was estimated to be 0.8, assuming the diffusion-control rate in 2-propanol[12] for k_{et}[CB]. This shows that 80% of the energy absorbed by acetone will be transferred to the ground-state CB. Therefore, the apparent yields obtained by using acetone as a sensitizer will afford the approximate quantum yields for dechlorination reactions from the excited triplet-state CBs. Table 1 makes it clear that the reactions from the excited triplet-state CBs take place. However, the dechlorinations of 2- and 3-CB are very inefficient compared with the quantum yields for dechlorinations obtained by the direct-excitation method, given in Table 2. Thus, the triplet contribution to their dechlorinations is considered to be negligibly small. This finding supports the conclusion obtained in the quenching experiments of 2- and 3-CB by 1,3-cyclohexadiene. The apparent yield of 4-CB sensitized by acetone is larger than that obtained in a direct-excitation method, but both yields are of the same order of magnitude (10^{-3}). Thus, a remarkable dechlorination from the excited triplet state of 4-CB was supported by the results of the sensitization reaction with acetone.

On the other hand, the apparent quantum yields of 4-CB sensitized by acetophenone and benzophenone are much lower than that sensitized by acetone. However, the efficiencies of energy transfer from these triplet ketones to 4-CB are presumed to be 0.7 and 0.6[13] for acetophenone and benzophenone respectively; these values are comparable to 0.8 of acetone.

TABLE 2. DIRECT PHOTOLYSIS OF CBs IN 2-PROPANOL SOLUTION[a–c]

Compound	Irradiation time t/min	Formation of Biph c/μmol dm^{-3}	Quantum[d] yield
2-CB	15	118	0.3
3-CB	60	7.4	0.0047
4-CB	120	5.0	0.0016

a) Excitation: 290 nm. b) Strength of incident light: $\approx 1.5 \times 10^{15}$ photons s^{-1}. c) Concentrations of CBs were 5.0–5.5 mmol dm^{-3}. d) Value determined from the average of two or more runs.

It must be kept in mind that these efficiencies were calculated on the assumption of a diffusion-control rate for the energy-transfer process. The triplet energy of 4-CB can be roughly estimated to be 269 kJ mol^{-1} from the phosphorescence spectrum. This triplet level is low enough to accept the energy at the diffusion-control rate from triplet benzophenone, which has the lowest triplet energy (298 kJ mol^{-1})[11] among the sensitizers used. However, it has been considered by some authors[1,3,14] that the occurrence of dechlorination in CB requires a higher energy than the triplet energy estimated from the emission spectrum. Therefore, from the results shown in Table 1 one can lead the conclusion that the triplet-energy level of 4-CB responsible for dechlorination lies between the triplet levels of acetone (330 kJ mol^{-1})[11] and acetophenone (310 kJ mol^{-1});[11] the assumption of diffusion control is not satisfied in the case of acetophenone and benzophenone.

Typical carbon-chlorine bond dissociation energies for aromatic compounds are reported to be about 356 kJ mol^{-1}.[15] Therefore, the dechlorination reaction from the excited triplet state of 4-CB would be endothermic. This is confirmed by the low quantum yield shown in Table 2.

Reaction Mechanism. The dechlorinations of 2- and 3-CB occurred from the excited singlet state, while that of 4-CB occurred from the excited triplet state. Biphenyl has a planar structure in the excited singlet state,[16] whereas it is twisted in the ground state in solution. 2-CB will suffer a large steric hindrance in the excited singlet state due to the presence of the chlorine atom at the 2-position, so the chlorine atom in the excited singlet state would be very labile. We have considered that the high reactivity of the chlorine atom at the 2-position is derived from this steric effect.[17] The racemization of 2′-methoxy-6-nitrobiphenyl-2-carboxylic acid is appreciably depressed by introducing the chlorine atom at the 3′-position,[18] this depression was interpreted in terms of the buttressing effect. Thus, the hydrogen atom at the 2-position of 3-CB will be pushed to the opposite direction by the chlorine atom at the 3-position, and the rotation barrier around the carbon-carbon bond between two phenyl rings will increase. This suggests that the same lability of the chlorine atom as that of 2-CB can be expected for the dechlorination from the excited singlet-state 3-CB. However, the reaction of 3-CB should be very inefficient compared with that of 2-CB, since the rotation barrier induced by the buttressing effect would be much lower than the barrier induced by the chlorine atom at the 2-position.

On the other hand, the dechlorination of 4-CB occurred predominantly from the excited triplet state. The reaction from the excited singlet state would not be important, since no steric effect is expected in the case of 4-CB.

References

1) T. Nishiwaki, T. Shinoda, K. Anda, and M. Hida, *Bull. Chem. Soc. Jpn.*, **55**, 3565 (1982).

2) L. O. Ruzo, M. J. Zabik, and R. D. Schuetz, *J. Am. Chem. Soc.*, **96**, 3809 (1974).

3) N. J. Bunce, Y. Kumar, L. Ravanal, and S. Safe, *J. Chem. Soc., Perkin Trans. 2*, **1978**, 880; N. J. Bunce, J. P. Bergsma, M. D. Bergsma, W. D. Graaf, Y. Kumar, and L. Ravanal, *J. Org. Chem.*, **45**, 3708 (1980).

4) J. I. G. Cadogan, *J. Chem. Soc.*, **1967**, 4257.

5) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

6) The excited singlet states of benzene and its derivatives are quenched at nearly the diffusion-control rate by diene (R. G. Brown, and D. Phillips, *J. Am. Chem. Soc.*, **96**, 4784 (1974)).

7) K. Tsujimoto and M. Ohashi, *Proc. Symp. Synth. Org. Chem. (Tokyo)*, June 1973, p. 70.

8) M. Ohashi, K. Tsujimoto, and K. Seki, *J. Chem. Soc., Chem. Commun.*, **1973**, 384.

9) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Am. Chem. Soc.*, **94**, 3679 (1972).

10) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York, (1973), p.198.

11) N. J. Turro, "Modern Molecular Photochemistry," Benjamin/Cummings, California (1978), Chaps. 8 and 10.

12) G. S. Parks and C. S. Caffee, *J. Phys. Chem.*, **31**, 439 (1927). The rate constant at diffusion control, (k_D) was evaluated to be 7.7×10^9 dm^3 mol^{-1} s^{-1} by means of this equation: $k_D = 8RT/3000\eta$.

13) To calculate these efficiencies, an ordinary value of k_D in 2-propanol (4.5×10^9 dm^3 mol^{-1} s^{-1}) was used because of the low concentrations of sensitizers in the 2-propanol solution. The k_d, k_h, and Φ_{iC} values of these triplet ketones are tabulated in 11).

14) P. J. Wagnar, *J. Am. Chem. Soc.*, **89**, 2820 (1967).

15) S. W. Benson, "The Foundation of Chemical Kinetics," McGraw-Hill, New York (1960), p.670.

16) I. B. Berlman, *J. Phys. Chem.*, **74**, 3085 (1970).

17) T. Nishiwaki, M. Usui, K. Anda, and M. Hida, *Bull. Chem. Soc. Jpn.*, **52**, 821 (1979).

18) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York (1962), Chap. 6.